INTRODUCTION TO

GENERAL INORGANIC CHEMISTRY

BY

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PREFACE

THIS book, the first draft of which was written six years ago, is the outgrowth of the introductory course in chemistry which the author has given for the past fifteen years. A subject undergoing the persistent, though unconscious criticism of keen minds should gain in self-consistency and coherence as it is presented year after year. For example, an answer must be found for the common question, "Why does the chemistry of the laboratory differ from the chemistry of the text-book and the lecture to such an extent that they seem to be different sciences?" The chemistry of the laboratory is, of course, the only real chemistry, and that of the lecture must be somewhere at fault. The student neither sees nor weighs atoms, for instance, and so the details of the laboratory experiment, which *are* seen and studied, become the basis of the whole treatment. The atom and the ion assume the rôle of merely figurative aids in the description of the facts. Gradually the conception of chemical equilibrium comes to contribute the major part of the explanation which is essential to the evolution of a *system of chemistry* founded upon experiment.

In the choice and arrangement of the material, several principles have served as guides:

The book is intended primarily for students beginning the study of chemistry in a college, university, or professional school. It is assumed that use of the book goes hand in hand with systematically arranged laboratory work in general chemistry. The first four chapters, for example, contain a discussion of a few typical experiments. They appeal directly to experience derived from the performance and observation of these and other similar experiments in the laboratory and in the class-room. In these chapters some of the features which are characteristic of every chemical phenomenon are sought out, put into words, and illustrated.

No conception is defined, and no generalization or law is developed, until such a point has been reached that applications of the conception and experimental illustrations, later to be related in the law, have *already* been encountered, and there is about to be occasion for further applications and illustrations of the same things in the chapters immediately succeeding. In these chapters the applications are frequent and explicit. Later, page references in parentheses continue to indicate the recurrence of examples which might otherwise fail to be noticed. It is one thing to come to *know* a principle of the science, and quite another thing to have acquired, by constant repetition of the process, a confirmed *habit of using* the principle on every appropriate occasion. To assist still further in the attainment of this end, an attempt is made in the last six chapters again to mention and illustrate, by way of review, the most important principles of the science.

No conception or principle is given at all, unless, in its most elementary aspects, it can be made clear to a beginner; and unless it is capable of numerous applications in elementary work; and, finally, unless a knowledge of it is of material use in organizing and unifying the result of such elementary work.

An attempt has been made to state the laws and to define the conceptions of the science in terms of experimental facts. The figurative language of hypothesis has been employed only in explanations.

Familiarity with physical conceptions and facts is so indispensable to the chemist that no apology is needed for the rather full treatment which some of them have received.

No two chemists would agree perfectly in regard to the apportionment of space. The processes of chemical industry, and the every-day applications of chemical science, cannot all be mentioned. These fields, and that of mineralogy, can be represented by examples, without the incompleteness of the result being in any way a detriment to a work of a general character. Again, a dense array of descriptive material, unillumined by explanation, is a positive injury to an introductory treatise. All reference to historical matters cannot be omitted, but a logical display of the subject can be achieved with comparatively

little of the history. Of all the aspects of the science, the theoretical is thus the one whose treatment is susceptible of least abbreviation.

The principles of chemical equilibrium are (and have been for the past half-century) fully as much required for intelligent consideration of the simplest experiment, as is the theory of combining proportions itself. Important parts of the theories of solutions and of the battery are much more recent, but each is equally indispensable to the understanding of matters which cannot long be withheld from the notice of the beginner. Surely space ought not to be saved by entire omission of essential parts of the chief thing that makes chemistry at all worthy of a place amongst the sciences. Nor may we attain brevity, no matter how great the temptation, by condensing the passages on theory until they reach the limit of comprehensibility by an expert. Without clear exposition, full illustration, and frequent application, laws and principles simply repel, or worse still, mislead the beginner.

We reach the same conclusion from another view-point. Every student should have access to, and should use, reference books devoted especially to descriptive, industrial, historical, and physical chemistry, and to mineralogy and crystallography — at least one good book in each of these five subjects. With the help of the index, the veriest tyro can find in a few moments, almost anything he wants in four out of five of these branches. But just the opposite is the case with the theory. Only an expert realizes what information he is in need of, and knows under what titles to look for it. And often even the expert would fail to understand the isolated sentence or paragraph when found. In a large proportion of connections the beginner simply cannot use such a book for rapid reference at all. In many lines, therefore, much may be left to outside reading, but for theory almost no dependence can be placed on reference work in other books.

For the reasons enumerated above, an unusually large proportion of space has been given to theoretical matters. The actual amount of theory is no greater than is usual in books of the same class, but the explanations are often fuller. Even so, the beginner will probably find that some parts form reading as stiff as any he is accustomed to undertake, without complaint, in physics or mathematics. It can only

be said that easily read modes of presenting the science of chemistry are apt to delude the beginner into thinking he has mastered the subject, when in reality he has simply been steered clear of the chief difficulties.

The order of topics was determined by many considerations, jointly. For example, in the first week of his work, a student may encounter experiments, in connection with which, almost every part of chemical theory might usefully be discussed. But mastery of the theory must necessarily come bit by bit, and the theory is therefore distributed through the book. Instead of being introduced as soon as a fragment offers a chance for explanation, the treatment of each of the various theoretical subjects, as far as possible, has been postponed until a whole chapter could be devoted to it. The result makes subsequent reference easier, and facilitates alterations in the order of study. Thus, the hypothesis of ions is not mentioned as soon as it well might be, because satisfactory treatment of it must follow the molecular and atomic hypotheses of which it is an extension, and because the full explanation of this hypothesis must be preceded by some account of the phenomena of electrolysis and of the essential properties of solutions, and, also, by a discussion of chemical equilibrium, a subject which of necessity presupposes two or three months' work in chemistry. There is another disadvantage which arises from a premature explanation of the hypothesis of ionization. When it appears at an early stage, too long an interval separates this subject from the study of the metallic elements, and the details are largely forgotten before the field for their chief employment is reached.

The paragraphs in smaller type are not intended for beginners, but for advanced students and teachers, which accounts for the fact that reference will frequently be found in them to subjects treated systematically in later chapters.

The exercises and problems are simply samples of some of the various kinds of questions which might be raised in dozens at the end of every chapter.

Recent works on general chemistry have been consulted during the revision of the manuscript. Of these A. A. Noyes' admirable *General*

Principles, Ostwald's *Grundlinien* — a veritable *tour de force*, and Bloxam's *Chemistry* may be mentioned as having proved most suggestive. The author owes special thanks to several friends who have undertaken the toilsome work of reading part or all of the book in manuscript or in proof, and in particular to his colleagues Messrs. Julius Stieglitz, H. N. McCoy, L. W. Jones, and E. S. Hall, to Dr. J. B. Tingle of Johns Hopkins University, to Mr. C. M. Wirick of the R. T. Crane High School, Chicago, and to Mr. Maurice Pincoffs of Chicago. The author alone is responsible for any defects which may be inherent in the plan of the book and for errors which may have escaped detection, but must gratefully acknowledge the very great benefit the book has derived from the friendly criticism of these gentlemen. Other corrections or suggestions will be gladly received by the author.

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CONTENTS*

CHAPTERS		PAGES
I.	**Introductory I**	3
	The Scientific Method — Three Illustrative Chemical Phenomena — Two Characteristics of Chemical Phenomena.	
II.	**Introductory II**	17
	Conservation of Mass — Energy — Applications of the Conception of Energy in Chemistry — The Progress of Chemical Actions Spontaneous or Forced — Chemical Activity and its Cause — Of Simple and Compound Substances — Some of the Fundamental Ideas Used by Chemists and the Corresponding Terms — Methods of Work and Observation in Chemistry.	
III.	**Introductory III**	41
	The Law of Definite Proportions — The Law of Multiple Proportions — The Measurement of Combining Weights — The Law of Combining Weights — Equivalents — Atomic Weights.	
IV.	**Introductory IV**	53
	Symbols, Formulæ, and Equations — Units of Measurement in Chemical Work — Calculations in Chemistry.	
V.	**Oxygen**	61
	Preparation of Simple Substances — Preparation of Oxygen — Physical Properties of Oxygen — Specific Chemical Properties — Chemical Properties of Oxygen — The Making of Equations Again — Oxides — Combustion — Oxidation — Means of Altering the Speed of a Given Chemical Action: By Change of Temperature — Rapid Self-sustaining Chemical Action and Means of Initiating It — Other Means of Altering the Speed of a Given Chemical Change: By Change in Concentration; By Catalysis; By Solution — Thermochemistry.	
VI.	**The Measurement of Quantity in Gases**	80
	The Variable Concentration of Gases — The Method of Allowing for Varying Concentration in Measuring Quantity in Gases — The Relation of the Volume of a Gas to Temperature — Mixed Gases — Densities of Gases — Vapor Densities of Liquids and Solids.	

* The titles of most of the descriptive paragraphs have been omitted from this table because it is easier to find matters of this nature by consulting the index. The titles of all the theoretical paragraphs, however, have been included.

CHAPTERS PAGES

VII. **Hydrogen** 92
Acids — Preparation of Hydrogen — Tests — Displacement — Valence — The Valence of Radicals — How to Ascertain the Valence of an Element or Radical — Physical Properties of Hydrogen — Diffusion — Chemical Properties of Hydrogen — A False Use of the Word "Affinity" in Explanation of Chemical Actions — The Speed of Chemical Actions: A Means of Measuring Activity.

VIII. **Water** 113
Natural Waters — Physical Properties of Water — Ice — Steam and Aqueous Tension — Chemical Properties of Water — Hydrates — Composition of Water — Gay-Lussac's Law of Combining Volumes.

IX. **The Kinetic-Molecular Hypothesis** 128
Kinetic-Molecular Hypothesis Applied to Gases — Critical Phenomena — Kinetic Hypothesis Applied to Liquids — Diffusion in Liquids — Kinetic Hypothesis Applied to Solids — Crystal Forms — Crystal Structure — Molecular Magnitudes — Formulative and Stochastic Hypotheses.

X. **Solution** 145
General Properties of Solutions — The Scope of the Word — Limits of Solubility — Recognition and Measurement of Solubility — Terminology — Solution one of the Physical States of Aggregation of Matter — Kinetic-Molecular Hypothesis Applied to the State of Solution — Kinetic-Molecular Hypothesis Applied to the Process of Solution — Independent Solubility — Solution of a Gas in a Liquid — Two Immiscible Solvents: Law of Partition — Influence of Temperature on Solubility — Phases — Equilibrium in a Saturated Solution — Metastable Condition — Saturation — Properties of Solutions Proportional to Concentration: Vapor Tension — Freezing-Points of Solutions — Densities of Solutions — Heat of Solution — Definition of a Solution — Application in Chemical Work.

XI. **Chlorine and Hydrogen Chloride** 168
Chlorine — Chemical Relations of the Element — Hydrogen Chloride — The Kinetic Hypothesis Applied to the Interaction of Sulphuric Acid and Salt — Classification of Chemical Interactions and Exercises Thereon — SUMMARY OF PRINCIPLES.

XII. **Molecular Weights and Atomic Weights** 190
Meaning of Avogadro's Hypothesis — Two Kinds of Laws in Science — The Relative Weights of the Molecules — The Relation between the Weights of Molecules and the Combining Weights: Atoms — The Choice of the Value 16 for the Atomic Weight of Oxygen — The Chemical Unit of Molecular Weight — The Chemical Molecule — The Gram-Molecular

CHAPTERS PAGES

(Molar) Volume — Determination of the Atomic Weight of Each Element — The Accepted Atomic Weights of the Elements — Molecular Formulæ of Compounds — Molecular Formulæ of Simple Substances — Molecular Weights of the Elements at Various Temperatures — Dissociation of Compounds — Chemical Interactions Studied by Observation of Volumes: Molecular Equations — Other Methods of Determining Molecular Weights — Properties Possessed by Atomic Weights, but not by Equivalents — Dulong and Petit's Law — Periodic System: Molecular Structure — Application to the Case of a New Element.

XIII. **The Atomic Hypothesis** 217

XIV. **The Halogen Family** 226
The Chemical Relations of Elements — The Chemical Relations of the Halogens — Bromine — A Plan for Making Very Complex Equations — Hydrogen Bromide — Iodine—Hydrogen Iodide — Fluorine — Hydrogen Fluoride — Association— The Halogens as a Family — Compounds of the Halogens with Each Other.

XV. **Chemical Equilibrium** 246
Reversible Actions — Kinetic Explanation — The Influence of Homogeneous Mixture — The Influence of Molecular Concentration — Law Connecting Molar Concentration and Speed of Reaction—The Condition for Chemical Equilibrium —The Effect of Changes of Volume on Chemical Equilibrium — Heterogeneous Equilibrium — Applications in Chemistry: Displacement of Equilibria by Changes Affecting Concentration — Affinity *vs.* Solubility — Displacement of Equilibria by Changes in Temperature: van 't Hoff's Law and Le Chatelier's Law — SUMMARY OF PRINCIPLES.

XVI. **Oxides and Oxygen Acids of the Halogens** 263
Compounds of Chlorine Containing Oxygen — Nomenclature of Acids and Salts — Salts and Double Decomposition — Hypochlorites and Hypochlorous Acid — Hypochlorous Anhydride — Hypochlorous Acid as an Oxidizing Agent: Bleaching — Thermochemistry of Hypochlorous Acid — Simultaneous, Independent Chemical Changes in the Same Substance — Chlorates — The Separation of Substances by their Solubility — Chloric Acid — Making of Equations Again — Chlorine Dioxide: Chlorous Acid — Perchlorates, Perchloric Acid, and Perchloric Anhydride — Oxygen Acids of Bromine — Oxides and Oxygen Acids of Iodine — Iodates and Iodic Acid — Various Acids Derived from One Anhydride — Periodates and Periodic Acid — Chemical Relations.

CHAPTERS PAGE

XVII. **Dissociation in Solution** 28

Some Characteristic Properties of Acids, Bases, and Salts, Shown in Aqueous Solution.

OSMOTIC PRESSURE: Phenomena Produced by Osmotic Pressure —The Phenomena a Logical Consequence of Semi-permeability — Measurement of Osmotic Pressure — Osmotic Pressure and Concentration — Osmotic Pressure and Temperature — An Analogue of Avogadro's Hypothesis — Determination of Molecular Weights — Osmotic Pressure and Dissociation in Solution.

DEPRESSION IN THE FREEZING-POINT OF A SOLVENT: Measurement of Freezing-Points — Laws of Freezing-point Depression — Determination of Molecular Weights — Freezing-Points and Dissociation in Solution — Boiling-Points and Dissociation in Solution — Comparison of the Results of the Three Methods.

THE APPLICATION OF THESE CONCLUSIONS IN CHEMISTRY: The Constitution of Solutions of Acids, Bases, and Salts — Nomenclature: The Ionic Hypothesis — Ionic Equilibrium — Appendix: Recent Measurements of Osmotic Pressure.

XVIII. **Ozone and Hydrogen Peroxide** 30

Ozone — Hydrogen Peroxide — The Interaction of Barium Peroxide and Sulphuric Acid — Thermochemistry of Hydrogen Peroxide — Peroxides: Chemical Constitution and Molecular Structure.

XIX. **Electrolysis** 31

Introductory — Chemical Changes Connected with Electrolysis — Ionic Migration — Relative Speed of Migration of Different Ions — Faraday's Laws — The Ionic Hypothesis — Difficulties Presented by this Hypothesis — Amounts of Electricity on the Ions — Résumé and Nomenclature — Actual Quantities of Electricity Concerned in Electrolysis —The Electrical Energy Required to Decompose Different Compounds — Polarization — Conductivity for Electricity — Degrees of Ionization of Common Substances: Acids, Bases, Salts — Degree of Ionization of Water — General Remarks on these Values — Comparison with the Results Obtained by Other Methods.

XX. **The Chemical Behavior of Ionic Substances** 33

Solutions of Ionogens are Mixtures — Each Kind of Ion in a Mixture Acts Independently.

SALTS, IONIC DOUBLE DECOMPOSITION, PRECIPITATION: Salts —Double Decomposition of Salts in Solution — Solution and Precipitation of Salts — Individual, Specific Chemical Properties of Each Ionic Material — Application in Chemical Analysis — Hydrolysis of Salts.

CHAPTERS PAGES

ACIDS AND BASES AND THEIR DOUBLE DECOMPOSITION WITH SALTS: Hydrogen Salts — Hydrion — Modes of Ionization of Acids — Activity of Acids — Salts of Hydroxyl — Hydroxidion — Ionic Double Decomposition and Precipitation of Acids and Bases — Ionic Double Decomposition and Activity.

NEUTRALIZATION: Acidimetry and Alkalimetry — Theory of Neutralization — Indicators — Neutralization of Little-ionized Substances — Thermochemistry of Neutralization — Volume Change in Neutralization.

MIXED IONOGENS AND DOUBLE SALTS: Acid Salts — Basic Salts — Mixed Salts — Double Salts.

KINDS OF IONIC CHEMICAL CHANGES: Disunion and Combination of Ions — Displacement of One Ion: Electromotive Series of the Metals — Destruction or Formation of a Compound Ion — Change in the Charges of Two Ions — Charge and Discharge of Two Ions, Electrically — Two or More Kinds of Ionic Action Simultaneously.

NON-IONIC MODES OF FORMING IONOGENS: Acids and Bases — Salts.

XXI. **Sulphur and Hydrogen Sulphide** 367
Sulphur — Hydrogen Sulphide — Sulphides — Polysulphides — The Chemical Relations of the Element Sulphur.

XXII. **The Oxides and Oxygen Acids of Sulphur** 378
Sulphur Dioxide — Sulphur Trioxide — Oxygen Acids of Sulphur — Sulphuric Acid — Sulphates — Constitution of Hydrogen Sulphate — Hyposulphurous Acid — Sulphurous Acid — Illustration of the Effect of Concentration on Speed of Interaction — Sulphites — Thiosulphuric Acid — Persulphuric Acid — Polythionic Acids — Sulphur Monochloride — Thionyl Chloride — Sulphuryl Chloride.

XXIII. **Selenium and Tellurium — The Periodic System** 401
Selenium — Tellurium — The Chemical Relations of the Sulphur Family — Metallic and Non-metallic Elements — Classification by Atomic Weights — Mendelejeff's Scheme — General Relations in the System — Applications of the Periodic System.

XXIV. **Nitrogen and its Compounds with Hydrogen** 415
Nitrogen — Ammonia — Ammonium Compounds — Hydrazine — Hydrazoic Acid — Hydroxylamine — An Active State of Hydrogen (Nascent Hydrogen) — Halogen Compounds of Nitrogen.

CHAPTERS PAGES

XXV. **The Atmosphere. The Helium Family** .... 42°
Components of the Atmosphere — Air a Mixture — Liquefaction of Gases — Liquid Air — Argon — Helium — Neon, Krypton, and Xenon.

XXVI. **Oxides, and Oxygen Acids of Nitrogen** 438
Nitric Acid — Nitrates — Nitric Oxide — Molecular Compounds — Nitrogen Tetroxide — Oxidizing Actions of Nitric Acid — Nitrous Acid — Nitrites — Nitrous Oxide — Explosives — The Principle of Transformation by Steps.

XXVII. **Phosphorus** 455
Phosphorus — The Electric Furnace — Phosphine — Phosphonium Compounds — Halides of Phosphorus — Oxides of Phosphorus — The Phosphoric Acids — Phosphorous Acid — Hypophosphorous Acid — Structural Formulæ of Salts of Hydrogen — Sulphides of Phosphorus — Comparison of Phosphorus with Nitrogen and with Sulphur.

XXVIII. **Carbon and the Oxides of Carbon** 473
Carbon — Calcium Carbide — Carbon Dioxide and Carbonic Acid — Carbonates — Rôle of Chlorophyl-bearing Plants in Storing Energy — Photochemical Action — Carbon Monoxide — Carbonyl Chloride and Urea — Carbon Disulphide.

XXIX. **Some Carbon Compounds** 490
The Hydrocarbons — Petroleum — Fractional Distillation — Methane — Organic Radicals — Ethylene — Acetylene — Benzene — Formic Acid — Acetic Acid — Oxalic Acid — Carbohydrates and Fermentation — Alcohols, Esters, and Ethers — Soap — Drying Oils — Cyanogen — Hydrocyanic Acid — Cyanates — Thiocyanates.

XXX. **Flame** 509

XXXI. **Silicon and Boron** 518
Silicon — Silicon Hydride — Carbide of Silicon — Silicon Tetrachloride — Silicon Tetrafluoride — Hydrofluosilicic Acid — Silicon Dioxide — Silicic Acid — Colloidal Solution — Silicates — Boron — Hydrides and Halides of Boron — Boric Acid — Borates — Boron Trioxide — Nitride and Carbide.

XXXII. **The Base-forming Elements** 530
Physical Properties of the Metals — General Chemical Relations of the Metallic Elements — Hydrolysis of Halogen Compounds, Used to Distinguish Metallic from Non-metallic Elements — Salts of Complex Acids — Classification of the Metallic Elements by their Chemical Relations — Occurrence of the Metallic Elements in Nature — Methods of Extraction from the Ores — Compounds of the Metals: Oxides and

CHAPTERS PAGES

Hydroxides — Compounds of the Metals: Salts — Solubilities of Bases and Salts — Hydrated Forms of Salts Commonly Used — Isomorphism.

XXXIII. **The Metals of the Alkalies: Potassium and Ammonium.** 548

The Chemical Relations of the Metallic Elements of the Alkalies — Potassium — the Hydride — Chloride — Iodide — Bromide and Fluorides — Hydroxide — Oxides — Chlorate — Bromate and Iodate — Nitrate — Carbonate — Cyanide — Sulphate and Bisulphate — Sulphides — Properties of Kalion: Analytical Reactions — the Spectroscope — Rubidium and Caesium — Ammonium Chloride — Ammonium Hydroxide — Nitrate — Carbonate — Sulphate — Sulphides — Microcosmic Salt — Ammonium Amalgam — Ammonion: Analytical Reactions.

XXXIV. **Sodium and Lithium. Ionic Equilibrium Considered Quantitatively** 569

SODIUM: Sodium Hydride — Chloride — Hydroxide and Oxides — Nitrate and Nitrite — Carbonate — Bicarbonate — Sulphate — Thiosulphate — Phosphates — Tetraborate — Silicate — Properties of Natrion: Analytical Reactions — Lithium.

IONIC EQUILIBRIUM CONSIDERED QUANTITATIVELY: The Simple Case — Excess of One Ion — Special Case of Saturated Solutions — An Illustration: Potassium Chlorate — Other Illustrations — Direction of a Chemical Change Determined by Ionic Concentrations. Rule for Precipitation or Solution of Insoluble Substances.

XXXV. **The Metals of the Alkaline Earths** 588

The Chemical Relations of the Elements — Calcium and its Compounds — The Phase Rule, a Method of Classifying All Systems in Equilibrium — Hard Water — Mortar and Cement — Interaction of Insoluble Salts with Acids — Precipitation of Insoluble Salts in Presence of Acids — Dissolving of Insoluble Salts by Solutions of Salts — Glass — Calcion: Analytical Reactions — Strontium and its Compounds — Barium and its Compounds — Analytical Reactions of the Calcium Family.

XXXVI. **Copper, Silver, Gold** 614

The Chemical Relations of the Copper Family — Copper and its Compounds — The Solution of Insoluble Salts when Complex Ions are Formed — Silver and its Compounds — Electro-plating — Photography — Gold and its Compounds.

XXXVII. **Glucinum, Magnesium, Zinc, Cadmium, Mercury. The Recognition of Cations in Qualitative Analysis** 641

CHAPTERS		PAGES
XXXVIII.	**Electromotive Chemistry** .... Factors and Units of Electrical Energy — Displacement Cells — Potential Differences Produced by the Metals Singly — Application to Cells — Other Applications: Couples: Concentration Cells — Electrolysis: Discharging Potentials — The Factors of Energy — Methods of Measuring Chemical Activity.	664
XXXIX.	**Aluminium and the Metals of the Earths** .... The Rare Elements of This Family — Aluminium and its Compounds — Dyeing: Mordanting — Kaolin and Clay: Earthenware and Porcelain.	681
XL.	**Germanium, Tin, Lead**	692
XLI.	**Arsenic, Antimony, Bismuth**	707
XLII.	**The Chromium Family. Radium** .... The Chemical Relations of the Family — Chromium — *Derivatives of Chromic Acid — Chromic Compounds* — Chromous Compounds — Analytical Reactions — Molybdenum — Tungsten — Uranium — Radium — The Discovery of the Element — Properties of Radium Compounds — *The Radiations of Radium Salts — The Decay of an Element.*	722
XLIII.	**Manganese**	737
XLIV.	**Iron, Cobalt, Nickel**	746
XLV.	**The Platinum Metals** .... Ruthenium and Osmium — Rhodium and Iridium — Palladium and Platinum.	763

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CHAPTER I

INTRODUCTORY I

HUMAN knowledge has become, in recent times, so extensive and complex that the truths ascertained have had to be divided, more or less arbitrarily, into groups. Thus, the study of animals, their classification by structure, life-history, distribution, and so forth, form the group known as zoölogy. Such a group is called a **science**, and includes a more or less distinct body of knowledge. That the boundaries of these groups are purely arbitrary, and do not exist in the subject-matter itself, is seen at once in our own treatment of them. Thus, for convenience, we take the structure of animals *by itself* and style it anatomy; but we include in the science of physiology the study of the way in which the parts *of both plants and animals* perform their functions; and we assemble cognate parts of two groups in sciences like astro-physics and physical chemistry. The sciences, therefore, are not mutually exclusive, and their boundaries overlap in every direction.

The difficulty in deciding what are the most convenient boundaries is as great with chemistry as with the other groups. At the one extreme we have the **abstract sciences**, logic and mathematics. At the other extreme lie the **concrete sciences** like geology, zoölogy, and astronomy. The former are not concerned primarily with the study of matter at all, but with that of abstract conceptions. The latter deal with definite aggregates of matter, such as the nature and history of a particular deposit of sulphur and their relation to those of other deposits of sulphur, or the structure and history of a particular collection of organic material known as a pike, and their relation to the structure and history of a mass of similar material called a salmon. Between these two sets of sciences are the regions occupied by the **abstract-concrete sciences**, physics and chemistry. These sciences deal in part with the same portions of matter, but in a more

abstract way than do geology or biology. To them, all specimens of pure sulphur are alike, whether they have been formed by volcanic action, or have been deposited by bacteria in an entirely different manner. In particular, the line which divides physics and chemistry from one another is often difficult to draw. It is assumed, however, that the reader is already familiar with the elements of physics, and so, in place of entering upon an academic discussion of the nature of this line, we shall allow its location to emerge as we proceed.

The same principle of grouping is pursued within each field. Thus the preparation and properties of chemical compounds is called *descriptive* chemistry, and the content of this portion of the subject is in turn classified according to a plan involving the consideration of the constituents of each compound. The study of the proportions of the constituents in compounds, of the conditions under which chemical action occurs, and related matters of a more abstract character, are grouped together in *theoretical* chemistry, which is likewise subdivided. Again, the means that have been devised for recognizing the components of mixtures or compounds and measuring their quantities constitute the several branches of *analysis*. The subdivisions of chemistry of this kind are numerous.

The ideal in view in thus classifying the content of a science is to convert it into an **organized body of knowledge**. The various ways used to organize the facts of a science will be presented in detail as opportunity offers. These ways constitute what is called the **scientific method**.

It is only by following intelligently the way in which the science is manufactured, step by step, out of the raw material furnished by observation and experiment, that the student can gain a sound foundation for more advanced work in the same science, or a mental training broad enough in its tendency to add measurably to his efficiency in every other task. The chief object of useful thought, no matter whether the problem is one of language, history, business, or life, is to organize isolated facts into knowledge, and the means of successfully accomplishing this is the use of the scientific method.

Chemical Phenomena: Their Most Obvious Characteristic. — Chemistry being primarily an experimental, and not a purely abstract science, we can best make our first approach to it through the consideration of some familiar chemical phenomena which shall serve as illustrations.

When clean iron is exposed to air and moisture it becomes rusty, first on the surface, and finally throughout its whole mass. The iron with which we start is a dark-gray, metallic-looking substance, which has a high specific gravity (about 7.5), is ductile, has great tenacity, and is readily attracted by a magnet. Rust, on the other hand, is a reddish or brownish substance which has an earthy appearance, is much lighter specifically than iron (sp. gr. about 4.5), is brittle, and is not attracted by a magnet. The phenomenon seems to have consisted in the gradual substitution of the second of these substances for the first.

The *chemical fact* here is that iron, when in contact with air and moisture, gives rust. Consideration will show, however, that we do not perceive this fact except by noting the *physical qualities* of the original and of the final materials. The data describing a chemical phenomenon consist in an enumeration of physical observations, like the above physical properties of iron and rust. It is, indeed, an invariable characteristic of every chemical phenomenon that our information is all derived from physical study of the materials. Thus, when a candle burns, it undergoes a chemical change, and we observe a solid, waxy substance disappearing progressively from view. A closer study of the facts shows that a mixture of gases is rising from the flame, and we find that the material of the candle is contained in this. Here, again, we use physical means of observation.

It is further true of these, as of all chemical phenomena, that the *physical properties* of the original and those of the final substances *are invariably entirely different*. We observe also that this sort of transformation is *always abrupt*. As the change spreads, the minute fragment of iron of one moment becomes the minute fragment of rust of the next, and is endowed at once with all the new properties in full measure. No part of the mass loses its magnetic qualities completely, for example, before it has reached the limit of change in color or tenacity. Since we are compelled to define the species of matter by their constant physical properties (see p. 35), the possession by two or more bodies of permanently different properties constitutes them *ipso facto* samples of different materials. We may, therefore, say, more briefly, that the products of a chemical change are recognized at once to be *new and different substances*.

Thus the **most obvious characteristic** of a chemical phenomenon is **that all the physical properties of the substances alter, that this alteration is abrupt, that, in fact, the products are different substances, and**

that the recognition and study of such a phenomenon is accomplished entirely by observations of a physical nature. Other characteristics, less obvious, but equally constant, will presently be brought to light.

The chemical phenomena which are familiar are innumerable. The burning of illuminating-gas or of kerosene, the coagulation of the white of an egg, the decay of animal and vegetable matter, the action of hard water on soap, the "burning" of limestone, and the slaking of quicklime, are examples. The reader should analyze these changes, applying the above criteria, and see for himself why they are classed as chemical.

So far as this first characteristic is concerned, some merely physical phenomena will be recalled, which are not unlike the rusting of iron. Thus, when water is raised in temperature, its properties begin to alter: it becomes more mobile, its specific gravity changes, its refracting power for light is modified, and so forth. At first, however, these changes proceed by imperceptible gradations and lack the abruptness of chemical change. But when 100° C. is reached the water passes into steam, and the whole of the properties of this gas are different from those of water. Conversely, by cooling, the water may be converted into ice, and again there is an abrupt and profound change in properties. On this account, some chemists would classify "changes of state" as chemical phenomena. More usually, however, the absence of the other characteristics yet to be mentioned is held to justify the more common view, and ice, water, and steam are regarded as identical, and not different substances.

The very language we use bears testimony to the universal acceptance of the view that a physical change does not constitute a fundamental alteration. Thus, we have solid *lead* and molten *lead*, *air* (the gas) and liquid *air*. In the case of water alone has it been found convenient to distinguish ice, water, and steam by separate names.

Fact and Generalization or Law. — If the preceding paragraph be reëxamined, it will be seen that a number of **facts** are mentioned in it. We begin the organization of knowledge according to the scientific method by trying to determine the facts. Thus, we find some specimens of iron are variously colored, and some are brittle. Examination shows, however, that the former peculiarities are due to paint, for example, and the latter to the presence of carbon and other foreign materials in the iron (cast iron). Finally, we ascertain the facts that iron itself is gray and tough.

Facts are the ultimate units of the structure of a science. Thus, a single isolated observation, no matter how accurately made, does not furnish us with the sort of fact that can receive a permanent place in our collection. It is only after much research and thought that we can ascertain which are the fixed elements in the variety of experience in any line, and so determine what are the facts, in the sense in which we have used the term.

Putting together a statement like that appearing in heavy type above, is the second step. We examine facts of a like kind, or pertaining to like phenomena, to see whether any general statement can be made that will cover some feature common to the whole of them. In the above illustrations, after settling the intrinsic properties of several substances, and then determining the facts about the way in which these properties are affected under certain circumstances, we decide that, when all the properties change abruptly in a permanent way, the cases in which this takes place shall constitute a distinct class, and we call them cases of chemical change. The statement which in a few words or phrases sums up those features of all the phenomena of like kind which are constant, is called a **generalization**. Often it is called a **law**: there is no decided difference in the usage of the two words. Sometimes it is described as a **principle** of the science. A **generalization** or **law** in chemistry, therefore, is a **brief statement describing some constant mode of behavior.**

Of course, the same set of facts may be viewed in many ways. Picking out the relationships which are most comprehensive and, at the same time, are best fitted to form part of still broader generalizations, or to take their places alongside of equally broad ones, requires the highest ability. The most important laws, like that describing the behavior of gases when compressed (Boyle's law), are usually connected with the names of the men by whom the relationships were discovered and the generalizations formulated.

The word "formulate," as applied to a law, is preferable to the word "discover." The latter is ambiguous and suggests that the law existed before it was found. Even the relation which it puts into words, did not, properly speaking, exist, because relations are picked out of a complex by the mind, and the particular relation selected is a property of the mind and not of the constituents of the complex itself.

The reader must beware of the misconception that a law *enforces* behavior in accordance with its tenor. The mere *statement* that every piece of matter attracts every other, cannot compel a stone to fall; nor can the mode of behavior of one falling stone persuade any other to do likewise. The law is simply a record of what is invariably observed to happen.

It is, therefore, also very misleading if we permit ourselves to say that Boyle's law "acts" so as to "cause" gases to behave in a certain way, or that the law "operates" to "produce" a certain behavior, or that other behavior is "impossible" to the gas, or that the law of cohesion "intervenes" when the gas is under

low pressure, and causes its behavior to "diverge from that required" by Boyle's law, or to say that a gas "disobeys" Boyle's law. In scientific discussions, such figures of speech are alone permissible as throw light on the subject. Phrases like the above, common as their use is, have been selected apparently with a view to introducing a maximum of distortion and obscurity. It is the gas that "acts" and gives rise to the making of Boyle's law, and the latter is only an epitome of the *way* it acts. Everything that may be conceived may also be possible in nature, although there are many things which have not yet been known to occur. Therefore, we may not say that it is "impossible" for a gas to alter its volume otherwise than inversely with the pressure. The progress of science would be almost completely arrested, if, every time we succeeded in formulating a seemingly satisfactory statement of truth in regard to some set of phenomena, the exhibition by nature of any behavior which was in conflict with our statement became forthwith "impossible." It is not the gas which "diverges" from our statement or "disobeys" our law, but our statement which is proved by the behavior of the gas to be inaccurate. Our procedure, in such cases, is always more logical than our language, for we never attempt to cure the gas of its error, but always the law itself by suitable modification in its phraseology.

The Explanation of Rusting. — In considering the complete disguise which is assumed by a substance that has undergone chemical change, the first question which arises is: Can we in any way account for this great and permanent change in properties which very generally distinguishes the chemical phenomenon from the physical? Some additional facts will be required before we can answer this question. Many attempts have been made, from the earliest times, to learn the exact nature of the change known as rusting. It was found that many metals besides iron underwent a somewhat similar alteration, and that, where the transformation did not occur spontaneously, heating prompted it. The first fact which seemed to throw light on the subject was the observation that a piece of metal becomes heavier when it rusts. This was noticed as early as 1630, by a French physician, Jean Rey. His work was done chiefly with lead and tin, the former of which gives a dirty yellow, and the latter, a white powder, on rusting. He inferred correctly from his experiments that contact with the air had something to do with this chemical change. Other investigations on the same subject were made by Boyle (1627–1691), Mayow (1645–1679), and Hooke (1635–1703), in England, and they led to the same conclusion. The increase in weight was to be accounted for, therefore, by the supposition that some material from the air had been added to the metal during the process. In other words, iron, for example, was one substance composed of iron only, and rust was another substance composed of iron and some other material taken

from the atmosphere; and, the two substances being different in composition, their properties might naturally be expected to differ. The substance taken from the air was subsequently named oxygen.

A rough imitation of the rusting of iron may be shown to be accompanied by an increase in weight. Iron powder is suspended by means of a magnet over one pan of a balance, and the equipoise is restored by placing small shot on the other pan. When the iron is heated, union with oxygen begins, and, after a time, the pointer inclines markedly to one side. The product here is magnetic oxide of iron (Fe_3O_4), however, and not rust (Fe_2O_3, xH_2O).

An Older View: Phlogiston. — Simple, and to a certain extent satisfactory, as this explanation appears to us, it must be said that it gained little sympathy from the contemporaries of these men. The other investigators had been prejudiced by a remarkable hypothesis which was supposed to explain both rusting and combustion. Starting with a suggestion of Plato's, that during combustion some material escaped from the burning body, and that the flames and heat represented the vigor with which this substance rushed out, Stahl and Becher invented the idea that a substance, which they called "phlogiston," was contained in all materials capable of rusting or burning. Its escape accounted for the phenomena of combustion, and its absence for the alteration in properties of the residual substance. They were perfectly aware that the material was heavier after rusting than before, but refused to sacrifice their hypothesis to a mere fact like this. So they ingeniously appended the suggestion that phlogiston was a substance which not only was not subject to gravitation, but possessed the opposite property of levity. Thus, its escape rendered the material from which it issued heavier than before. Instead of demanding the preparation and examination of phlogiston itself, and the demonstration that it weighed less than nothing, the generality of chemists of that age accepted the idea without proof. It is not surprising, therefore, that many of their attempts to explain chemical phenomena on the basis of an arbitrary assumption like this should have proved confusing and infertile. The fact that foreign matter was actually gained by a body during the process of rusting was not generally accepted until it was demonstrated anew by Lavoisier (1774). He showed that a portion of the air really disappeared when tin rusted, and that the increase in weight of the tin corresponded with the loss in matter of the air. The whole development of chemistry was stunted by the general belief in the conception of phlogiston

and, during the one hundred and fifty years which passed between Jean Rey's discovery and Lavoisier's, relatively little progress was made.

The introduction of the balance into the chemical laboratory, and the first use of measurements of weight as a means of exploring and explaining chemical changes, is frequently ascribed to Lavoisier. As a matter of fact, it is difficult to state when measurement of weight first became the chief ally of the chemist in his work. Important and conclusive results were obtained by its means, however, before the time of Lavoisier, for example, by Jean Rey, Boyle, and Black (1728–1799).

Explanation in Science. — The word **explanation**, which was employed repeatedly in the last two sections, is used in science as the name of a definite process. It stands simply for **a description in greater detail**. Thus, when, to the acquaintance with the outward manifestations of rusting, we are able to add the further description that it is produced by the union of oxygen from the air with iron, we feel increased satisfaction, and we say that an explanation has been found. Sometimes we get this satisfaction by an explanation which is a description, not of additional facts, but of some imaginary condition which takes their place in our thought. The hypothesis (or supposition) of phlogiston was somewhat of this nature (see Formulative hypothesis).

There is no such thing as a final explanation. At the very next step, when we ask why the union of oxygen and iron produces a body that is red and non-magnetic, we are compelled to say we do not know. Even a supposition in regard to how this happens is as yet lacking.

An explanation in science never professes for a moment to give the reasons for any occurrence. We simply do not know *why* behavior in nature is as it is. Hence statements like that in regard to union with oxygen, constitute all the answer that we can give to the question with which a recent section (p. 8) opened.

Three Illustrative Chemical Phenomena. — Since oxygen is an invisible gas, the demonstration that rusting consists in the union of this gas with a metal, requires somewhat complicated apparatus. The next illustration, while lacking historical interest, is simpler, because both substances are visible, and are easily handled.

Iron unites, not only with oxygen from the air, but also, with almost equal ease, with sulphur. To study the behavior of the materials we must know their properties. The properties of iron we have already

enumerated (p. 5). Sulphur is a pale-yellow substance of low specific gravity (sp. gr. 2). It is easily melted (m.-p. 115° C). and, although it does not dissolve in water, it may be dissolved completely in carbon disulphide (41 : 100 at 18°).* It crystallizes in rhombic forms (Fig. 1). Now, when iron filings and powdered sulphur are rubbed together in a mortar, the product, although it has a different color from either of the constituents, is still really composed of the two original kinds of matter, side by side. With the help of a microscope and a needle, they can be picked apart completely. By manipulation of the mixture with a magnet, we may remove some of the iron without much difficulty.

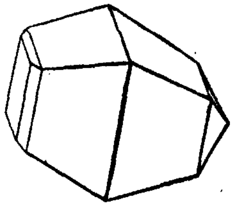


FIG. 1.

Again, using the solubility of sulphur in carbon disulphide and the insolubility of iron, we may shake the mixture with this liquid in a test-tube, and so dissolve out the sulphur (Fig. 2). When the contents of the tube are poured on to a filter (Fig. 3), the liquid (the **filtrate**) runs through, carrying all dissolved matter with it, and leaving undissolved matter behind. The former may be allowed to evaporate (Fig. 4), when yellow crystals of rhombic outline will be found to be the *sole residue*. The dark material remaining on the filter, when dry, is *wholly* attracted by a magnet. All these facts convince us that the properties of the components are still unaltered, and that, therefore, no chemical change has occurred.

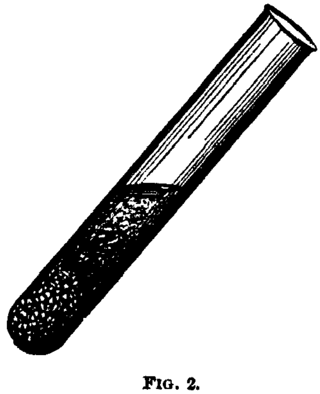


FIG. 2.

If we now put some of the original mixture into a test-tube and warm it, we soon notice a rather violent development of heat taking place, the contents begin to glow, and what appears to be a form of combustion spreads through the mass. The heating employed at the start falls far short of accounting for the much greater heat produced. When these phenomena have ceased, and the test-tube has been allowed to

* This expresses the fact that 41 parts, by weight, of sulphur dissolve in 100 parts, by weight, of carbon disulphide at 18° C.

cool, we find that it now contains a somewhat porous-looking, black solid. This material is brittle; it is not magnetic; it does not dissolve in carbon disulphide; and close examination, even under a microscope, does not reveal the presence of different kinds of matter. This substance is known to chemists as ferrous sulphide, and, as we see, its properties are *entirely different from those* of the constituents.

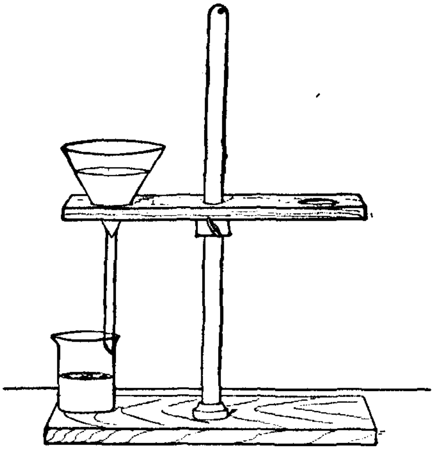


Fig. 3.

A substance formed in this way by the union of other materials is called a **compound**. The rusts given by various metals are therefore compounds also.

The **second illustration** is selected on account of its historical interest. One of the earliest chemical changes in which a gas, recognized to be distinct from air, was observed among the products, was noticed by Priestley (1774).* The observation was made with mercuric oxide, a bright red, rather heavy powder. When this substance is heated (Fig. 5), we find that a gas is given off, which is easily shown to be different from air, since a glowing splinter of wood is instantly relighted on being immersed in it. The gas is pure oxygen.† We notice also during the heating that a sort of mirror appears on the sides of the tube. As this shining substance accumulates it takes the form of globules, which may be scraped together. It is, in fact, the metal mercury, or quicksilver. If the heating continues long enough, the whole of the powder eventually disappears, and is converted into these products.

Fig. 4.

* An English nonconformist minister who occupied his leisure time with experiments in chemistry. He afterwards moved to the United States, and died in Northumberland, Pa.

† Air (*q.v.*) is a mixture of which only one-fifth is oxygen.

The extensive nature of the change in properties in this case is evident. It should also be observed that continuous heating is required to maintain this change in operation. It differs markedly from the iron and sulphur case in this respect. When the flame is removed, the evolution of oxygen ceases. The significance of this will appear shortly.

The **third and last example** is taken purposely in order to illustrate the variety of ways in which chemical change may be carried out. It is the interaction of silver nitrate and sodium chloride (common salt). The substances may be recognized by the form of the crystals of which they consist. The latter is composed of small cubes (Fig. 6), while the former presents a less familiar form geometrically (Fig. 7). Both substances are capable of being dissolved in water and, for this experiment, portions of each substance are shaken in separate vessels with water, until none of the solid remains. When the solutions are now poured together, we observe that the clear liquids at once become opaque, and that a dense mass of white, solid material appears suspended in the mixture (Fig. 8). This white substance consists of an extremely fine powder without any observable crystalline form. We know at once that it must represent a new substance, since it would not have appeared had it been soluble in water like the two materials from which it was made. We continue adding the one liquid gradually to the other until no further formation of this solid takes place, and then stop. By filtration (Fig. 3), we obtain the insoluble material (the **precipitate**) upon the filter paper, and the clear liquid (the **filtrate**) passes through and is caught in the vessel below.

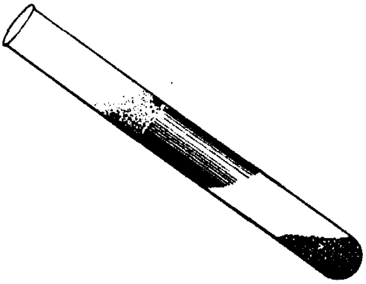


FIG. 5.

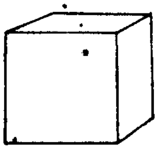


FIG. 6.

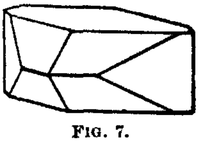


FIG. 7.

We are confronted with two possibilities: either both the original materials have come together to form one white insoluble material, or some other product (or products) may be present in addition to it. In the latter case, search must evidently be made in the liquid. By evap-

orating the *filtrate* in a suitable vessel (Fig. 4), we find that the second assumption represents the fact, for a considerable quantity of a white crystalline substance remains. The homogeneous character of this shows that there was but one product in solution, while the same property of the precipitate shows that there are but two products altogether.

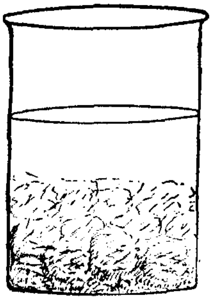


FIG. 8.

The insoluble material is composed of silver and chlorine, and it is known as silver chloride. Like some other compounds of silver, it darkens on exposure to light, turning first purple and then brown, and being decomposed by this agency into its constituents. The soluble solid obtained from the filtrate, we recognize as identical with a mineral, sodium nitrate, which is found in Peru. Its crystals are rhombohedral (Fig. 9). They resemble cubes which have been slightly distorted by pressing inwards two opposite corners. A strict investigation of all four substances shows that the following statement presents the facts in regard to the nature of the change: — Nitrate of silver, consisting of silver, nitrogen, and oxygen, with sodium chloride, consisting of sodium and chlorine, have changed into silver chloride, consisting of silver and chlorine, and sodium nitrate, consisting of sodium, nitrogen, and oxygen. This change presents several features which distinguish it from the previous ones: it is much more complex; it takes place in the presence of water; it requires no heating for its promotion; and the change is complete the instant the materials have been mixed, while the others required a good deal of time for their accomplishment.

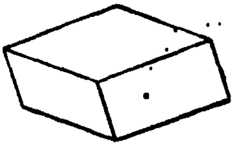


FIG. 9.

The Kinds of Chemical Change. — Having these three cases before us, — and they are types of most chemical phenomena, — we now proceed to analyze them, and so take another step towards explaining (*i.e.*, describing in detail) the nature of a chemical phenomenon. In the iron and sulphur experiment two materials were used, and a different one with new properties was produced. Here, in chemical language, the first two substances united or underwent **combination**. The rusting of iron, lead, and tin belongs also to this class. In the second illustration one material was used, and it was driven apart by

heating so that two new ones arose. A chemical phenomenon of this kind is called a **decomposition**. The last was the most complex, but a little examination shows that it does not present any novel features. The statement we gave (p. 14) about the way in which the constituents were distributed, before and after the change, shows that the original materials were altered by decomposition, and that the products were formed by recombination of these on a different plan. A third variety of chemical change consists, therefore, in the **concurrence of both of the first two kinds** in the same action. As several different varieties of this sort of complex redistribution of material can be distinguished, a distinct name is given to each. The present is called a **double decomposition** or metathesis.

When we encounter other chemical changes, we shall find the extent of the stride we have taken in this critical analysis of a few examples. It will then appear that the chemical changes of matter are not nearly so various as we might have anticipated. In fact, there are few changes which cannot be placed in one of the above categories. Those that cannot be so placed belong to a fourth sort of change which, for the sake of completeness, may now be mentioned.

It occasionally happens, especially in the case of compounds of carbon (see Urea), that one single kind of material turns into another single kind of material. Nothing is added and nothing removed, yet the new substance has different properties in every respect from the old. Most of those substances whose transformation is definitely assigned to this class contain several constituents, but a rough notion of this sort of chemical change may be obtained by considering the two forms of phosphorus. One of them is pale yellow in appearance, easily melted, and very easily ignited; the other is red, does not melt on being heated, and is difficult to ignite. The latter is made from the former by heating it continuously for some hours in a closed vessel at about 300°. As no material is taken up, the weight of the substance is unchanged, and yet, when the vessel is opened, the common phosphorus is found to have turned into the red variety. As the foregoing paragraphs show, we have good reason to believe that the properties of a substance are intimately related to its constituents. Carrying out this idea, the hypothesis (or suggestion) has been made that, since here also the properties change, there must be some readjustment of the material, even in cases like this. Hence, we designate changes of this kind **internal rearrangements**.

In the completeness of the transformation, and in the fact that only one original substance and one product are required, the physical changes of the nature of melting a solid and vaporizing a liquid resemble the fourth variety of chemical change. Where, then, is the line between chemistry and physics to be drawn? It is in this fourth group only that the difficulty is encountered. All agree that warm solid phosphorus is chemically identical with cold phosphorus. Nearly all scientific men at present assign the study of the melting and the vaporization of phosphorus and other substances to physics. Some chemists consider the solution of phosphorus in carbon disulphide or some other solvent (it is practically insoluble in water), although the material is recovered unchanged by evaporation of the liquid, as a chemical change. But the great majority regard this as physical also. If not chemically different, the solid, liquid, gaseous, and dissolved forms of a substance must be classed as mere physical states of aggregation. On the other hand, red phosphorus is held by most chemists to be chemically different from yellow phosphorus. Many kinds of matter show as much variety in form as phosphorus, and some show more.

In solving an ordinary puzzle, we work knowing that some simple solution exists. When studying nature, we are saved much embarrassment by remembering that, in cases like this, we are not seeking for a clear-cut distinction of whose existence we are assured in advance. Nature is under no obligation to furnish easily classifiable facts at all. The limitations of our minds compel us to classify as far as we are able to do so. On this plan alone can we master the infinity of detail. But the resulting system exists in our own minds, where it originated, and not in nature. In the present instance, we are seeking, as always, to make a distinction for our own convenience. But, at present, the effort to make a final distinction that can be used consistently causes more inconvenience than the alternative of letting the matter rest. The history of previous experiences leads us to hope that, with fuller knowledge, we shall be able, sooner or later, to construct a system of classification even for this obscure region.

The Second Characteristic of Chemical Phenomena. — We are now able to make another generalization (or condensed statement of fact): **In chemical phenomena substances enter into combination, come out of combination, or change their associates in combination or their state in the compound.** In other words, **the material changes its *composition or its constitution.***

This generalization furnishes an explanation of the former (p. 5) to a certain extent. Each individual substance has its own composition and its own set of physical properties. Hence, when, by chemical transformation, substances of new and different composition are produced, the materials must simultaneously acquire the specific properties of the new substances.

Summary. — Thus far, we have learned that chemistry deals with the changes in composition and constitution which substances undergo, and with the alteration in properties which accompanies and gives evidence of those changes.

CHAPTER II

INTRODUCTORY II

If we now return to the three illustrations of chemical phenomena which we have been studying (pp. 10–14), we shall find a new question arising naturally out of them. This is, whether the *mass* of the materials is altered, as are the other attributes, in these chemical changes.

Third Characteristic of Chemical Phenomena: Conservation of Mass. — The most painstaking chemical work seems to show that, if all the substances concerned in the chemical change are weighed before and after the change, there is no evidence of any alteration in the quantity of matter. The two weights, representing the sums of the constituents and of the products respectively, are, indeed, never absolutely identical, but the more careful the work and the more delicate the instrument used in weighing, the more nearly do the values approach identity. We are able to state, therefore, as a **third characteristic** of all chemical phenomena, that **the mass of a system is not affected by any chemical change within the system.**

This statement simply means that the great law of the conservation of mass holds true in chemistry as it does in physics. Chemical changes, thoroughgoing as they are in respect to all other properties, do not affect the mass; an element carries with it its weight, entirely unchanged, through the most complicated chemical transformations. This is the only attribute which persists.

A law, as we have seen (p. 7), is a condensed statement describing some constant mode of behavior. It is simply a summary of our experience. As such, it is subject to modification when a fact is discovered with which it conflicts. Thus, it is perfectly possible that we may yet find cases of demonstrable changes in weight accompanying other physical or chemical changes in a limited system. Indeed, it has more than once been alleged that such changes have been observed. It used to be a law that the earth was flat. It is now more correct to say that a limited area of perfectly level ground is *very nearly* flat.

It will be observed that the phrasing of the above law carefully limits its scope to amounts of matter such as are dealt with in laboratory experience. We have no evidence on which to make any statements about the mass of matter in more extensive chemical changes. A common form of the law, to the effect that

"the mass of matter in the universe is unchangeable in amount," is not a law at all, in the only sense in which the word is used in science. It is a statement in regard to supposed facts which are almost entirely beyond our experience. It is, therefore, a proposition of a transcendental (that is, transcending experience) nature, and has its proper place in metaphysics. Astronomical observation, it is true, has as yet furnished no evidence of changes in the mass of our own or other celestial systems. But, absence of evidence to the contrary, especially considering the relatively limited scope of our knowledge, both in respect to space and time, is far from being proof of the correctness of the proposition.

Superficial observation, as of a growing tree, might seem to give evidence of the very opposite of conservation of matter. But here the carbon dioxide gas in the air, the most important source of nourishment for plants, is overlooked. Similarly the gradual disappearance of a candle by combustion seems to illustrate the destruction of matter. But if we insert sticks of sodium hydroxide in a U-tube (Fig. 10) to catch *the gases* which rise through the flame, we find that the gases weigh even more than the part of the candle which has been sacrificed in making them. When we take account of the weight of the oxygen obtained from the air which sustains the combustion, we find that there is really neither loss nor gain in weight. If we carry out chemical changes in closed vessels (Fig. 11), which permit neither escape nor access of material, we find that the weight does not alter.

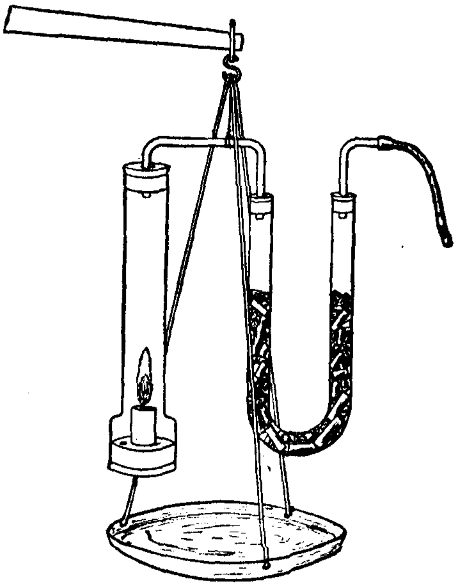


FIG. 10.

One way of stating the difference between chemistry and physics is to say that changes in which both the mass and the identity of the substance are conserved belong to the latter, while those in which the mass alone is conserved belong to chemistry.

Physical Concomitants of Change in Composition. — Study of the three typical chemical changes described in the last chapter may now be resumed, in order to see whether anything further of a general nature is characteristic of such phenomena. We recall at once that a prominent feature of the union of iron and sulphur was the **heat** which, as shown by the glow spreading through the mass, seemed to be developed after the action was once started. It is found that many chemical changes are like this one, in exhibiting simultaneously the production of very perceptible amounts of heat. On the other hand, the decomposition of mercuric oxide, as was pointed out (p. 13), owed its continuance to the persistent application of heat, and ceased so soon as the source of heat was withdrawn. Here, apparently, heat was consumed during the progress of the change, and the chemical action was limited by the amount of heat supplied. The **production or consumption of heat** may, therefore, be a feature of chemical change.

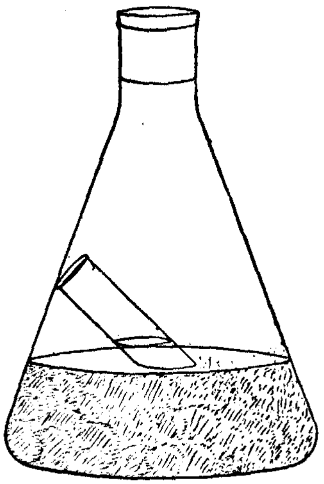


FIG. 11.

In the iron and sulphur case, as in other chemical actions where the heat developed is great, **light** also was given out. In the last of the three actions, on the other hand, we obtained a substance (silver chloride), which may be kept for any length of time in the dark, but, by the action of sunlight is broken up into its constituents (p. 14). It would appear, therefore, that **light may be given out or used** in connection with chemical change. Noting these facts stimulates us to look for other similar concomitants of changes in composition.

If we dip two wires from a battery or dynamo into a solution of nitrate of silver (Fig. 12), such as was used in the third experiment, we observe the instant production of a coating of silver on the negative wire. By preparing the solution properly and allowing the **electricity** to flow through it for a sufficient length of time, all of the compound can be decomposed and all its silver deposited. It is needless to say that this release of the silver from chemical combination and liberation of the metal at the electrode, goes on only so long

as the current of electricity is employed, and that electricity is consumed in the process. *Very many substances can be decomposed in this way.*

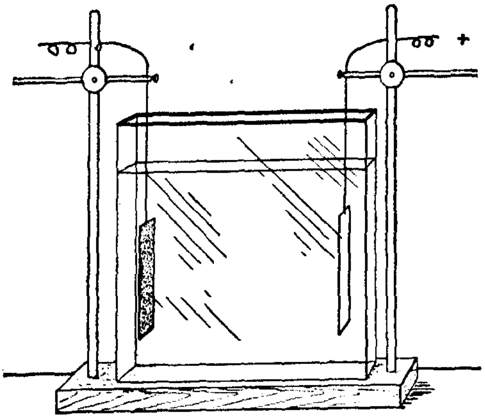


FIG. 12.

The inverse of this is likewise familiar. If we place in dilute sulphuric acid a stick of the metal zinc, we find that a gas is given off rapidly (Fig. 13), that the zinc gradually dissolves, and that a large amount of heat is developed. Under favorable circumstances, the liquid may even rise spontaneously to the boiling-point. This form of the action produces heat. If, however, we attach the same stick of zinc to a copper wire, and, having provided a plate of platinum also connected with a wire, immerse the two simultaneously in the acid (Fig. 14), then a galvanometer, with which the wires are connected, shows at once the passage of a current of electricity round the circuit. Exactly the same chemical change goes on as before. The sole difference is that the gas appears to arise from the surface of the platinum. It is easy to show, however, that the platinum by itself is not acted upon by dilute acids, and, in this case, undergoes no change whatever; it serves simply as a suitable conductor for the electricity. Here, then, in place of the heat which the first plan produced, we get electricity. The arrangement is, in fact, a battery, for a battery is a system in which a chemical action which would otherwise give heat furnishes electricity instead. Thus, **electricity may be consumed or produced in connection with a change in composition.**

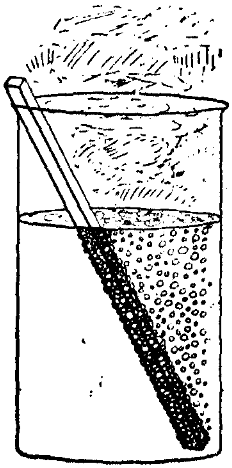


FIG. 13.

Even violent rubbing in a mortar, in the case of some substances, can effect an appreciable amount of decomposition in a few minutes.

In this way silver chloride can be separated into silver and chlorine, just as by light. It is the **mechanical energy** which is the agent, and part of it is *consumed* in producing the change, and only the balance appears as heat. Conversely, the *production* of mechanical energy, as

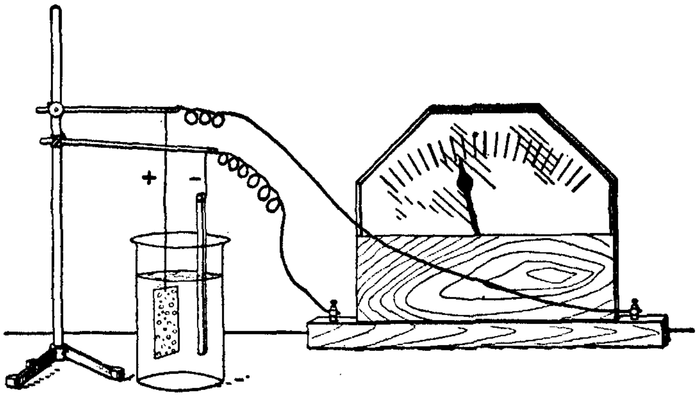


FIG. 14.

the result of chemical change, is seen in the behavior of explosives and in the working of our muscles. Thus, **mechanical energy may be used up or produced** in chemical changes.

Summing our experience up, we may state that no change in composition occurs without some concomitant, such as the production or consumption of heat, light, electricity, or, in some cases, mechanical energy.

Classification of the Concomitants of Change in Composition: Energy. — The problem of classifying (*i.e.*, placing in a suitable category) things like heat, light, and electricity has occupied much attention. They do not possess mass. In all changes in composition, one of these natural concomitants is given out or absorbed, sometimes in great amount, yet, in none is any alteration in weight observed. Nor may these concomitants be overlooked, simply. A conception is a real thing; a religious belief may be most real and potent. There are many things which are real, although they are not affected by gravitation. In the present instance we reason as follows:

A brick in motion is different from a brick at rest. The former can do some things that the latter cannot. Furthermore, we can

easily make a distinction in our minds. The brick can be deprived of the motion and be endowed with it again. Thus, we can get the idea of motion as a separate conception. Similarly, we observe that a piece of iron behaves differently when hot, and when cold, when bearing a current of electricity, and when bearing none. We conceive then of the brick or the iron as having a certain amount and kind of matter which is unalterable, and as having motion, heat, or electricity added to this or removed. Thus, we describe our observations by using two categories, one of which includes the various kinds of **matter**, and the other, various things whose association with it seems to be invariable and is often so conspicuous.

At first sight, these concomitants of matter seem to be quite disparate. But a relation between them can be found. If the heat of a Bunsen flame or of the sun is brought under a hot-air motor (Fig. 15) violent motion results. Again, if the motor is connected with a dynamo, electricity may be generated. Still again, if the current flows through an incandescent lamp, heat and light are evolved. Conversely, when motion is impeded by a brake, heat appears. When a current of electricity is run through the dynamo, motion results. But the most significant facts are still to be mentioned. The heat absorbed by the motor is found to be greater when the machine is permitted to move and do work, than when it is not. Thus, it is found that when work is done some heat disappears, and is, in fact, transformed into work. Similarly, when the poles of the dynamo are properly connected and electricity is being produced, and only then, motion is used up. This is shown by the effort required to turn the armature under these circumstances, and the ease with which it is turned when the circuit is open. So, with a conductor like the filament in the lamp, unless it offers resistance to the current and destroys a sufficient amount of electricity, it gives out neither light nor heat. Finally, motion gives no heat unless the brake is set, and effort is then demanded to maintain the motion. These experiences lead us to believe that we have here a set of things which are funda-

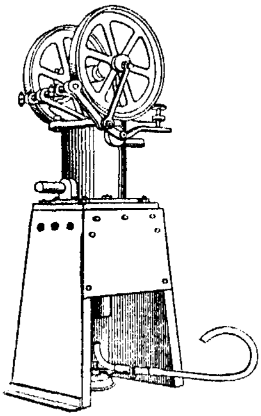


FIG. 15.

mentally of the same kind, for each form can be made from any of the others. We have, therefore, invented the conception of a single thing of which heat, light, electricity, and motion are forms, and to it we give the name **energy**: **energy is work and every other thing which can arise from work and be converted into work** (Ostwald).

Closer study shows that equal amounts of electrical or mechanical energy always produce equal amounts of heat. There is never observed any loss in any of the transformations of energy any more than in the transformations of matter. Hence, J. R. Mayer (1842), Colding (1843), and Helmholtz (1847) were led independently to the conclusion that **in a limited system no gain or loss of energy is ever observed**. This brief statement of the results of many experiments is called the law of the **conservation of energy**.

A current form of this law, namely, that "the total amount of energy in the universe is a constant quantity," is open to the same objection as the correspondingly flamboyant form of the law of conservation of mass criticized above. It has a more effective sound than the one we have given. Unfortunately, it is not only immensely in excess of any statement that present results of scientific work can justify, but is probably far beyond the limits of possible scientific observation. Scientific statements of fact can never err by being too conservative.

Matter and Energy as Concepts, and Definitions of the Latter. — The foregoing paragraphs about energy bring up the question of its relation to matter. This relation can be made clear only by a somewhat elaborate discussion of our fundamental conceptions.

The only real, first-hand knowledge which we possess, is that of our states of consciousness. All else, consisting, for example, of the way in which we interpret and describe our experience, is constructed out of our heads, so to speak. Now, we become aware of certain things which we call sensations, and seek to construct a mode of correlating and describing them. Our universal habit is to speak as if they were produced by something outside our minds, and so we begin the manufacture of an external universe. In course of doing this, we encounter some things which seem to occupy no particular space, which move from object to object, and possess no weight. One of these affects our eye, or a piece of chloride of silver, for example, yet escapes touch, and passes through glass as easily as through a vacuum. After consideration of our experience with this sort of thing, some of which has been detailed above, we decide that we shall posit the existence of energy.

Other things we encounter which appeal to the sense of touch and seem to possess more definitely located qualities, including weight. Another conception is needed to account for these; so we establish the category of matter.

Thus, we make shift to describe our sensations by the help of these two constructs, much as in analytical geometry we describe the location of a point by means of two coördinates. Energy and matter are, therefore, products of thought and not, primarily, objective realities. In chemistry, however, we always speak

of them objectively. Historically, the order in which these two concepts were named and defined was the opposite of that in which they stand above. Yet attempts to organize a conception, corresponding to energy, in response to a need of which thinkers were conscious, were not wanting before the nineteenth century opened. To go no further back than the days of phlogiston, we can easily perceive a certain resemblance between this concept and that of energy. The idea that heat was an "imponderable" had its origin much earlier, and shows the existence of the same effort to find a second fundamental conception different from matter.

There is much confusion of thought in many of the current definitions of energy. For example, it is often said to be "that which causes change in matter." This definition is not easy to bring into harmony with common experience in chemistry. Thus, when heat is applied to mercuric oxide, the change follows. But with iron and sulphur, the union of the two substances is a condition antecedent to the evolution of heat. It is as often true that change in matter causes the manifestation of energy as the reverse. Matter and energy are on the same plane. They are conceptions used jointly in describing what we observe. Neither is secondary to the other. We do not consider any particular one of the coördinates in geometry as secondary to the other, or as being affected by the other.

The recent theory of chemical potential and of the factors of energy (*q.v.*) seeks once more to ascribe the tendency to change (physical or chemical) in matter to the state of the energy associated with it. It is, therefore, incidentally, so constructed as to favor the definition just given.

The definition that "matter is the vehicle of energy" is obviously just as difficult to harmonize with the above mode of deriving the two conceptions. One axis is not spoken of as the vehicle of the other in geometry.

The innate desire to reduce our distinct categories to the smallest possible number may be seen in the history of this subject. The ancients sought the amalgamation of the two by regarding heat and light as imponderable forms of *matter*. In some quarters it is now believed that the one conception of *energy* is sufficient, and that matter may be put into the same category as being, for example, composed of minute particles of electricity (electrons).

The conception of *ether* was devised because those of matter and energy did not suffice for the description of all the phenomena of light. It is on the same plane with matter and energy. Lord Kelvin's effort to reduce the three categories to two (energy and ether) by assigning the rôle of matter to vortices in the ether is familiar to students of physics.

Application of the Conception of Energy in Chemistry. — At first sight it looks as if the statement that energy is conserved is not applicable in chemistry. Heat and electricity, for example, seem to be produced and consumed, in connection with changes in composition, in a mysterious manner. We trace light in an incandescent lamp back to the electricity, and this in turn to the mechanical energy, and this again to the heat in the engine. But what form of energy gave the heat developed by the combustion of the coal under the boiler, or

by the union of iron and sulphur in our first experiment? Since we do not perceive any electricity, light, heat, or motion, in the original materials, and yet wish to create an harmonious system, we are bound to conceive of the iron and the sulphur, and the coal and the air, as containing another form of energy, which we call **chemical** or **internal energy**. Similarly, when heat is used up in decomposing mercuric oxide, or light in decomposing silver chloride, we regard the energy as being stored in the products of decomposition in the form of chemical energy.

The Actual Quantities of Different Kinds of Energy which may be Obtained from a Fixed Amount of One Kind.— It will render all the above clearer if we give some numerical illustrations: A kilogram of water after falling (in a vacuum) 428 meters (about one-fifth of a mile), under gravity, possesses 428 kilogram-meters of mechanical (kinetic) energy. When the motion is arrested, the energy of motion is transformed into heat and raises the water one degree centigrade in temperature. We describe this amount of heat as 1000 calories (small); that required to warm one gram of water one degree (between 0° and 100°) being called one calorie. A kilogram of any other falling material would give the same amount of heat (1000 cal.), although, of course, if its specific heat were smaller than that of water, the temperature to which it would be raised would be higher, and *vice versa*.

Here the acting force is the attraction of gravitation, which is a special case. In absolute units, 1 g. falling 1 cm. generates energy enough to do 981 ergs of work. So that the thousand grams falling 428 meters, generates

$$1000 \times 42{,}800 \times 981 = 42{,}000{,}000{,}000 \text{ ergs of energy.}$$

The erg being so small, we often use the joule (=10,000,000 ergs). This amount is the same as 4200 joules.

Now, any body of the same mass, moving with the same final velocity, however set in motion, will also possess the same energy and give 1000 cal. The final velocity in the above case is $\sqrt{2gs} = 9{,}164$ cm. per second. The energy of motion ($\frac{1}{2}mv^2$) of one thousand grams of matter moving with this velocity is $= \frac{1}{2} \times 1000 \times (9164)^2 = 4200$ joules, as before. If the source of mechanical energy were a hot-air motor (or an engine) of one horse-power, then, since one horse-power represents a development of 746 joules per second, the 4200 joules of energy would be produced in about $5\frac{1}{2}$ seconds by this means.

If, instead of being turned into heat, all the energy of motion had been converted into electricity, the quantity of the latter would have illuminated a 16 candle-power incandescent lamp for 84 seconds (=1.4 minutes). Such a lamp requires the value of 50 joules per second of electricity and, therefore, in 84 seconds uses up the $50 \times 84 = 4200$ joules of energy. As an engine of 1 horse-power produces this amount of energy every $5\frac{1}{2}$ seconds, such an engine, if none of the energy were lost, could maintain nearly 15 lamps of this kind.

Finally, if the 4200 joules of electrical energy were applied to decomposing nitrate of silver in ordinary aqueous solution, it would liberate $6\frac{3}{4}$ grams (about $\frac{1}{4}$ oz.) of silver from combination.

Considerations Connected with Chemical Energy: Free Energy. — These conclusions compel us, for the sake of consistency, to think of all our materials as repositories of energy as well as of matter, each of these constituents being equally real and equally important. A piece of the substance known as "iron" must thus be held to contain so much iron matter and so much chemical energy. So sulphur contains sulphur matter and chemical energy. Thus, by a *substance* we mean a distinct species of matter, simple or compound, with its appropriate proportion of chemical energy.

Since a chemical phenomenon involves a change in the condition of both the matter and the energy constituents, both have to be considered in describing the transformation. Thus, in the first of the three experiments (p. 10) we must say that certain weights of iron matter and sulphur matter, each with a different but definite quantity of chemical energy, constituting the substances iron and sulphur respectively, are transformed into iron-sulphur matter with the same total weight, but less chemical energy, constituting the substance ferrous sulphide, with liberation of an amount of energy, chiefly in the form of heat, equivalent to the diminution in the quantity of chemical energy. As the chemical energy which may be liberated from the same substance differs in amount according to the material with which the substance is interacting, the total content cannot be stated. We can measure only the amount transformable in a given chemical change, and we call it the **free energy** which is available under the given circumstances. The above action may be represented more compactly, thus:

Iron, free Ch.E + Sulphur, free Ch.E ⟶ Ferrous sulphide + Heat E.

That the ferrous sulphide still contains chemical energy is shown by the fact that it interacts with many substances with further liberation of heat. At each step, however, the stock of energy in the material becomes smaller and the chemical activity less.

The Fourth Characteristic of Chemical Phenomena. — In the course of this discussion it has become clear that it is a characteristic of a chemical phenomenon that, besides a change in the state of the *matter*, **there is always an alteration in the amount of chemical energy in the system. This alteration consists in the production of chemical energy from, or the transformation of chemical energy into, an equivalent amount of some other form of energy.**

The absorption or liberation of energy accompanying a chemical transformation of matter is often, of the two, the more important feature. We do not burn coal in order to manufacture carbon dioxide gas. We are glad to get rid of the material product through the chimney. It is the heat we want. We do not employ zinc in batteries with the object of making zinc chloride or zinc sulphate. So we use

the electricity, and throw the products away when we refill the jars. It is the same with burning illuminating-gas or magnesium powder when we want light, and with eating food, which we do, chiefly, to get energy to sustain our activity. We do not run electricity for hours into a storage battery in order to make a particular compound (lead dioxide, for example), but in order to save and store the energy for future use. Fully half the total amount of chemical change used in industry and life is set in motion by us, exclusively, on account of the energy changes it involves.

As will be seen in the two following sections, observation of the amount of the energy absorbed or liberated in chemical changes is also of the greatest importance in the *scientific* study of chemical phenomena.

The Progress of Chemical Actions Spontaneous or Forced: Fifth Characteristic.—It will be recalled that iron and sulphur, when the interaction has once been started, continue to unite (p. 11) spontaneously until the chemical change is complete. Similarly, zinc interacts with dilute sulphuric acid (p. 20) until one of the substances is exhausted. On the other hand, mercuric oxide continues to decompose only so long as it is heated. Now, the first two actions liberate energy in the form of heat or electricity, while the latter consumes it. A study of all chemical changes shows that a distinction can be drawn on these lines between those which proceed spontaneously and those which do not. It is, in fact, a **characteristic of chemical phenomena** that, **in those actions which proceed spontaneously to completion, the free internal energy in the system diminishes by transformation into some other form of energy.**

This is a particular case of a principle which applies to all changes, both physical and chemical. All spontaneously occurring phenomena are accompanied by loss of energy. A stone falls, losing potential energy, but never rises spontaneously; a body cools, losing heat, etc.

The form of energy liberated in a chemical change which proceeds spontaneously is most commonly heat. Hence, **exothermal actions**, as those which produce heat are called, are usually of the spontaneous order, and **endothermal actions**, which absorb heat, generally are not. There are, however, numerous exceptions to this rule, both in physical and in chemical phenomena. Thus, water evaporates spontaneously, although in doing so it absorbs heat. There is a loss of energy in other ways more than sufficient to offset the acquisition of heat. So,

also, very many substances dissolve spontaneously in water and absorb heat in doing so. Phosphonium chloride (*q.v.*) decomposes spontaneously into phosphine and hydrogen chloride, although heat is thereby rendered latent. Ammonium carbonate (*q.v.*) spontaneously gives off ammonia, although in this chemical change heat is absorbed.

In any chemical change which proceeds spontaneously, the energy liberated may take the form of electricity when the materials are arranged so as to constitute a battery.

Chemical Activity. — Actions in which there is a relatively large loss of chemical energy, and, therefore, a considerable liberation of heat or electrical energy, proceed rapidly; that is to say, in them a large proportion of the material is changed in the unit of time. Those in which less free energy is transformed proceed more slowly. The speed of the chemical change, and the quantity of energy available because of it, are closely related. Now, we are accustomed to speak of materials which, like iron and sulphur, interact rapidly and with liberation of much energy as "chemically active." Thus, **relative chemical activity** may be estimated (1) by observing the speed of a change (see Speed of chemical actions), or, in many cases (2) by measuring the heat developed (see Thermochemistry), or (3) by ascertaining the electromotive force of the current the change gives, when arranged in the form of a battery (see Electromotive chemistry). These different methods will be discussed in later sections.

It is evident that the chemical activity of a given substance will not be the same towards all others. Thus, iron unites much more vigorously with chlorine than with sulphur, and, with identical amounts of iron, more heat is liberated in the former case than in the latter. With silver, sodium, and many other substances, it does not unite at all. One of the tasks of the chemist is to make such comparisons as this (see Specific chemical properties, p. 67). Evidently, the substances containing the most chemical energy will be in general the most active.

The "Cause" of Chemical Activity. — The reader will undoubtedly be inclined to inquire whether we can assign any cause for the tendency which substances have to undergo chemical change. Why do iron and sulphur unite to form ferrous sulphide, while other pairs of elements taken at random will frequently be found to have no effect upon one another under any circumstances? This question

is so likely to occur to the reader that it should be dealt with at once. The answer is that we do not know. Questions like this have to go without answer in all sciences. What is the cause of gravitation? We know the facts which are associated with the word — the fact that bodies fall towards the earth, for example — but why they fall we are unable to say. So, with chemical change, we can state all the facts we know about it, but even then we cannot say *why* it takes place.

The words "affinity" and "attraction" are sometimes advanced as if they supplied some explanation of chemical activity. Now, we have seen that an explanation in science (p. 10) is a description of the details of some process, either in terms of known facts, or by the use of some imaginary but plausible and helpful machinery. Here no facts are known. Even imaginary machinery has not yet been conceived by any one. So that these terms are words simply, and do not meet either of the conditions required of an explanation. They are names for "the tendency to undergo chemical change," and that is all.

All nouns, such as table or book, are general terms applicable to many more or less various individuals. Some special nouns are used in chemistry. For example, *affinity* names the tendency to undergo chemical change, and distinguishes this tendency by name from cohesion, or the tendency to unite physically. *Catalysis* names a kind of chemical change in which some specific substance must be present, yet itself undergoes no change. *Dissociation* names the kind of chemical change in which decomposition occurs with rise in temperature, and recombination when the temperature falls. But none of these terms, as such, is an explanation. It does not explain the concussion of two railway trains to name it a collision.

Of course, if we have some genuine explanation, applicable to all the other known cases of a class, any newly discovered example falls heir at once to this explanation. This would be true of a dissociation, where the kinetic theory and the law of mass action describe the details of all such phenomena. Here the explanation lies, not in the name, but in the knowledge we have of other instances of the same behavior. The name, of course, suggests the whole theory, if such a theory exists. But with affinity, or the tendency to enter into chemical action, we have no theory for any of the samples of the class. We are entirely ignorant as yet of the details of its mode of operation, equally so in every case, and, in fact, know nothing at all about it save that affinity exists and that we can measure its intensity. So the name cannot remind us of any explanation, for none has been suggested.

As words, the best one can say of them is that they are rather unfortunately chosen. Affinity suggests kinship, sympathy, or affection. But the suggestion that such human emotions control the behavior of iron and sulphur is too wild and too remote from common sense to furnish any assistance. Attraction hints at some preëxisting bond of a material kind which draws the substances together, for we cannot conceive of action at a distance without some intervening medium of communication. But we have no other evidence of the existence of an instantaneously adjustable harness capable of drawing materials into chemical action. It is harder to reduce this idea to comprehensible shape than to do without it.

If we are sometimes inclined to think that these are more than class-words, and do suggest some explanation, we have only to carry the same idea further to be landed in absurdity. Using similarly crude analogies, we might suppose that the elements were guided by scent, like dogs, or by sight, like birds, or by feeling, like fish, and so on *ad infinitum*, and forget that the fact itself was after all much simpler than the explanation. Affinity is simply a fanciful name for a real thing.

"Cause" in Science. — The word "cause" was employed in the heading of the last section, and it will be observed that no cause was found. This is the invariable rule in physical or chemical phenomena. We know of no causes, in the sense in which the word is commonly employed.

The word has only one definite use in science. When we find that thorough incorporation of the three materials is needed to secure good gunpowder, we say that the intimate mixing is a cause of its being highly explosive. By this we simply mean that intimate mixture is a *necessary antecedent* of the result. **A cause is a condition or occurrence which always precedes another condition or occurrence.**

Misuse of the word "cause" is frequent. The law of gravitation is not the cause of the behavior of falling bodies. It is simply a condensed narration of the facts about falling bodies, and was made long after the first bodies fell. Affinity, or the tendency to interact chemically, is the imagined antecedent of chemical change. Such causes, if we call them causes at all, are invented by way of supplying antecedents to things that appear to lack them, that our sense of symmetry may be satisfied withal. They are occasionally useful. But the less fiction we employ in the science, the less will be the danger that the student will mistake fictions for facts, or even fall under the delusion that it is a habit of science to spend more thought in making gratuitous assumptions than in ascertaining facts.

Of Simple and Compound Substances. — If we place before a physicist samples of iron, ferrous sulphide, and sulphur, he will report that there are three absolutely distinct *substances* represented, because they show three different sets of physical properties. A chemist, on the other hand, while admitting the accuracy of the report, in view of the criterion used by the physicist, which indeed he uses himself (*cf.* p. 5), will insist that there are only two perfectly distinct *kinds of matter* in the set, because he can make the second from matter furnished by the other two. The same sharp contrast in the points of view arises when mercury, mercuric oxide, and oxygen, or any similar set of substances, is submitted to the same two tribunals. In a sense, chemistry reduces the kinds of different matter to a much smaller number than does physics or any of the other sciences, and so it is the final authority in all questions involving matter. By the

chemist; dozens of physically distinct substances are regarded as closely related because they all can be made with iron, or when decomposed give it; hundreds are alike in that sulphur enters into their composition; thousands are compounds of oxygen. In fact, the number of kinds of matter which are perfectly distinct in the strictly chemical point of view is quite limited.

The conception contained in the last statement was not reached until centuries of effort had been spent in trying to make gold out of pyrite (a shining yellow mineral), silver out of lead, and similar fruitless tasks. The first to put our modern view into definite language was Lavoisier in his *Traité de Chimie* (1789). His investigations had already entirely overthrown the hypothesis of the phlogistians (p. 9), and had been based upon simple ideas of combination or decomposition of different kinds of matter. His work showed that decomposition had its limits. Mercuric oxide could be decomposed into mercury and oxygen, but no means was found of breaking these up in turn and producing any fresh substances from them. The kinds of matter composing these simple materials he named **elements**. The element is to be regarded as an ultimate chemical individual just as the substance is the physical individual. The definition of an element is therefore: **a distinct species of matter which has not been shown to be composite.**

The caution which prompted Lavoisier to use, as he did, the words "not *yet* been," was justified by the fact that several substances, in his time regarded as elementary, were afterwards shown to be compound. Thus, quicklime was a simple substance until Davy, in 1808, prepared the metal calcium and showed that quicklime was a compound of this metal with oxygen. Discoveries similar to this have been made on more than one occasion since.

Until recently a body made up of one or more specific elements had never been found to yield any simple substance different from those used in preparing it. In other words, one element had never been turned into another. And this is still true so far as the familiar elements are concerned. Experience with radium (*q.v.*), which seems to decompose and give helium, however, may lead to a revision of the conception of an element. Indeed, even the more radical hypothesis, that all the so-called elements are made of one fundamental material, has never lacked supporters. Perhaps the recent discoveries in regard to electrons will lead to the conclusion, already formulated by J. J. Thomson, that the kinds of simple matter differ only in the number and arrangement of the corpuscles constituting their atoms.

Element and Simple Substance Not Equivalent Terms.—We have seen that all substances, that is, physical individuals, must be thought of as containing both matter and energy (p. 26). It is certain that iron, if it could be deprived of the energy it loses in combining with sulphur, would be, before combination, as different from the free metal iron as is the compound ferrous sulphide itself. Now the development and use of the idea of elements just given, shows that by the word "element," applied to iron, for example, the chemist refers only to the *matter* of this specific variety. It is this part alone which passes *unchanged* from the state of metallic iron into combination and *vice versa*, or from one state of combination to another. ***An element* is therefore a kind of *matter* which *never exists alone*. It is always combined with more or less *chemical energy*, and often with some other element or elements as well.** ***A simple substance***, on the other hand, like all substances, **has independent existence, and contains but *one element* combined with a certain quantity of *energy*. *A compound substance*, or compound, contains *more* than one element together with a certain amount of energy.**

That this interpretation of the habit of thought of chemists is correct is shown by the fact that they speak of both the yellow and the red form as "the element phosphorus," and also describe phosphorus pentoxide and phosphine as "containing the element phosphorus." The only thing that is common to all four is, of course, *matter* of a specific variety, to which, therefore, the term "element phosphorus" must primarily apply. The individuality, marked by certain specific properties, of the yellow or the red variety or of one of the compounds *as a substance* is as much dependent on the energy it contains as on the matter. Hence the term *substance* covers the energy as well as the one or more kinds of matter contained in the material.

Having regard to this distinction, an element was defined above as a "variety of matter," and not as a substance, and the phraseology used throughout the paragraph maintains this distinction. No mention was made of energy in the definition or elsewhere, for, in comparing simple substances and compounds in the abstract, the only distinction is in the matter. Following each simple variety of matter into and out of combination, or from one state of combination to another, is one of the tasks of the chemist. It is also his business to observe the energy changes. But this is an exercise quite distinct from the other, and constitutes a separate task in which different methods of observation have to be employed.

The element is thus an abstraction, reached by leaving the energy out of consideration and thinking of the matter only. It is invented for the purpose of describing the difference between the concretes, the simple substance and the compound substance. To use element and compound as if *they* were the concrete things to be contrasted, involves confusion by mixing two distinct categories.

As we have only one name for the element and the corresponding simple substance, it is well, when there is danger of ambiguity, to call the ***simple substance***, not "iron," "sulphur," or "the element," but *free iron*, *free sulphur*, and in gen-

eral terms the *free element*, or the *elementary substance*. The same kinds of matter in *combination* are then *the element iron* or *combined iron*, and the *element sulphur* or *combined sulphur*.

The chemist's work is directed wholly by the thought that the individual element (the matter), after combination, is still present in the compound in some form which is at least *quasi*-discrete. The readiness of the element to be released once more under suitable conditions seems to favor this point of view. But with the energy in a substance it is different. We cannot easily think of the portions of this, which came in with the several constituents, as being any longer attached to particular parts of the compound. Indeed, in some actions (chiefly exothermal) the free energy diminishes and a part escapes, while in others the reverse occurs. Whatever energy the compound contains, it possesses as a whole, and a state of distribution between the constituents is seldom taken into consideration. The speculations concerning the relations of the atoms in complex molecules, which have played a large and useful part in organic chemistry, seem to constitute the only notable divergence from this point of view.

These remarks are introduced because they help to demonstrate the logical necessity of the chemist's habit of maintaining a sharp separation, in his mind at least, between questions involving changes in the state of combination of *matter* and questions of energy (see Formulæ and equations, p. 57).

Among the substances which we have been handling, iron, sulphur, mercury, oxygen, and hydrogen are the free forms of elements. On the other hand, the substances which we have shown to be composite are ferrous sulphide, rust, mercuric oxide, silver nitrate, and common salt. It will be seen that by combination of a *limited* number of elements, two, three, or four together, in varying proportions, all the known distinct substances might easily be accounted for. The list of elements whose individuality has been established appears upon another page (Chap. xii); of these the larger number are not frequently encountered. More than 99 per cent of terrestrial material is made up of eighteen or twenty elements, of which the quantities of the first eleven, as estimated by F. W. Clarke, are given in the following table:

Oxygen	49.98	Calcium	3.51	Hydrogen	0.94
Silicon	25.30	Magnesium	2.50	Titanium	0.30
Aluminium	7.26	Sodium	2.28	Carbon	0.21
Iron	5.08	Potassium	2.23		99.61

The evidence of the spectroscope shows that the sun and stars contain many of the very same elements as does the earth.

Some of the Fundamental Ideas used by Chemists and the Corresponding Terms. — To the chemist it is above all important that he should be able to describe in unambiguous terms the phenomena he observes and the inferences he draws.

To do this he requires some fundamental ideas connoted by suit-

able terms. Many of these ideas and terms we have been employing in order to accustom the reader to their use. It is now advisable to take them up more systematically.

Any particular specimen of matter, such as a piece of sulphur, a portion of water, a piece of ferrous sulphide, a fragment of granite, or some nitrate of silver solution, we call a **body**. There are thus as many bodies as there are discrete portions of matter. A body may be heterogeneous, or made up of visibly unlike parts, as granite and a **mixture** of iron powder and sulphur are; or it may be homogeneous, or alike in all parts, as are pieces of sulphur and ferrous sulphide and portions of water and nitrate of silver solution.

Examination of these homogeneous bodies shows that the sulphur, ferrous sulphide, and water differ from the nitrate of silver solution in having but one **physical component**, while the last contains two components, nitrate of silver and water, separable by physical means. The last is like a mixture, only it is homogeneous. Again, the first three differ amongst themselves, the first being a simple body, with one **chemical constituent**, and the two others being compounds having each two chemical constituents. We speak of the *components* of a mixture or a solution because the parts are *laid together* and retain in the former case all, and in the latter much, of their identity. But of a compound we use the word *constituents* because the parts are *built into each other* and have lost their identity.

When a body, say a specimen of sulphur, contains *a little* of some other physical component, we speak of it as **impure** sulphur. This does not mean that it contains dirt in the ordinary sense of the term. A little magnesium chloride is a common impurity in table salt (sodium chloride), and, by absorbing moisture, renders it more moist in damp weather than it would otherwise become. "**Chemically pure**" means that the quantities of the impurities which the material is most apt to contain have been reduced below the amount which would interfere with the most exact chemical work for which the substance is commonly employed. Absolutely pure bodies are unknown.

By convention we continually speak of "*pure*" hydrochloric acid, or of "*pure*" sulphuric acid, although there may be more than 60 per cent of water present in the former, and 7 per cent in the latter. By this we mean to distinguish the former, for example, from "commercial" hydrochloric acid, which contains impurities like sulphuric acid and a coloring matter in addition to the water. The water is in fact disregarded, since it is assumed to be present in all cases.

We distinguish one body, say one piece of sulphur, from another by its weight, form, or volume. Each particular specimen differs from every other in these **attributes.** These are general attributes possessed by matter and are used in chemistry for measuring quantity.

When all the bodies to which we should apply the name "sulphur" are compared, we find that, although some are in fine powder, and others in lumps of various shapes or in crystals, and thus differ in weight, form, and volume, they nevertheless have many qualities in common. These qualities we call **specific properties**, or properties common to a species. The material composing all the bodies of one species we call a **substance**. Some of the specific properties characterizing a substance and common to all specimens of one species are color, odor, crystalline structure, hardness, melting-point (temperature of fusion), solubility in water or other solvents, boiling-point (temperature above which, at 760 mm. pressure, the substance is gaseous), specific gravity, specific heat, and conductivity for electricity. Thus, sulphur is yellow, has little odor, crystallizes in the rhombic system, has a hardness of 2.5 on a scale of ten, has the m.-p. 115° C., is not perceptibly soluble in water but dissolves in carbon disulphide (41 : 100 at 18°), has the b.-p. 448° C., the sp. gr. 2, the sp. ht. 0.18, and is a very poor conductor. In the first two chapters, while presenting the experimental facts required for our discussion, we have had to speak of *substances* very frequently (*e.g.* pp. 26 and 32), and have done so always in the above sense.

Slight variations from the standard properties of the substance usually indicate the presence of an impurity homogeneously incorporated. The precise ways in which the properties are affected in such cases will be considered under solutions.

The "substance" will be seen to be of an *abstract* nature. It is a conception built up by selecting (or abstracting) the properties common to all specimens. Hence we classified chemistry as an abstract-concrete science (p. 3). The *bodies* under observation are *concrete*, the *classification of the results* is under conceptions of an abstract nature like this one.

That all bodies of a like kind have many identical properties is the most fundamental fact in chemistry. Being a general fact, we call it a law, and word it as follows: **The specific properties of a substance are constant in all specimens.** Experience having given us confidence in its universality, we take it for granted in all our work (*cf.* First characteristic, p. 5).

There are still other qualities which a body (or specimen of matter) may possess. It has, for example, a certain temperature, pressure, motion, or electric charge. These we speak of as **conditions of**

the body rather than properties. In the use of the body they may be altered, and some of them may be removed or added, arbitrarily.

Thus there are three kinds of qualities to be considered. The *attributes*, like weight, form, and volume, do not belong to substances but to bodies. The *specific properties*, like color, solubility, and odor, belong by right to substances, although we sometimes speak of them in connection with bodies. The *conditions*, like temperature and motion, belong to neither, for they can be altered without changing either the body or the substance.

When the word "properties" is used in speaking of a substance, we generally refer to the specific properties only, for a substance is by definition the bearer of nothing but constant, that is, unchangeable qualities. The weight and volume, the temperature and pressure, are variable, and they do not enter into the conception of the substance. This distinction sets the abstract nature of the "substance" in high relief.

Methods of Work and Observation in Chemistry.—It is not the end of chemical work to make generalizations or laws, like the characteristics of chemical phenomena (pp. 5, 16, etc.), or conceptions, like those dealt with in the preceding paragraph. These are simply the *means* by the help of which chemical work, whether it be investigation, commercial analysis, or manufacturing, may be carried on more systematically. Together they constitute our system for classifying the facts with a view to ready reference. The sample experiments (pp. 10–14), if reëxamined, will show that we there employed most of the categories of our classification which have so far been described.

Thus, in the experiment with iron and sulphur (p. 10), it was first our object to find out whether the bodies had interacted chemically on being mixed. To do this we endeavored to ascertain whether any portion of the mixture had acquired new specific properties (p. 35). Here we used the law (p. 7) that all the properties of the products of a chemical interaction are different (pp. 5–7) from those of the initial substances. We also noted the specific properties of the substances concerned, purposely omitting all mention of quantity and temperature, because attributes (p. 35) like the former and conditions (p. 35) like the latter do not characterize substances (p. 35) in general, as distinct from particular specimens, and cannot be used for identification. We found that a part dissolved in carbon disulphide and the remainder was all magnetic.

While all the specific properties, of which a few are mentioned on p. 35, find application in identification, the first seven in that list are

most frequently used. And of these seven the solubility in various solvents and the boiling-point are by far the most important. This is because they are best suited for *separating* mixtures. Thus, here, we first *removed* the sulphur by dissolving it, and then, after evaporating away the solvent, we completed the identification by recognizing the color and form of the residue. Similarly we recognized by its appearance and magnetic property the iron that was *left undissolved.*

Separation by the use of one of these two properties, *then* application of the others for identification, is the general order of procedure in chemistry. Most of the other properties cannot be recognized readily in *mixtures*, as a moment's thought will show. The general color and the specific gravity of a mixture, containing unknown substances in unknown proportions, for example, tell us little about the corresponding properties of the components. Magnetic properties may be used for separation, also, but iron is almost the only substance which shows them markedly, so that their application for the purpose is very limited.

The use of the boiling-point (temperature of vaporization) for separation was illustrated in the evaporation of the carbon disulphide to get the sulphur alone. This solvent has a very low boiling-point (46° C.) and therefore a high vapor pressure at the temperature of the room. By virtue of this it evaporates rapidly. The sulphur (b.-p. 448° C.) is not volatile under these conditions and remains behind.

In connection with this investigation we employed several of the common methods of **manipulation** used by the chemist. These methods are derived from the conceptions described in last paragraph. Thus we **treated the mixture with a solvent** (Fig. 11), on the assumption that if it was heterogeneous (p. 34) the components would each behave as if alone present. We then **filtered**, a method invented for dealing with a heterogeneous mixture consisting of a solid and a liquid. **Decantation** is often used in such cases when the solid is specifically much heavier than the solvent and settles readily. We allowed the carbon disulphide to **evaporate** spontaneously, and this is our favorite method of dealing with a mixture which is homogeneous, and therefore would run through a filter as a whole without suffering separation. When the liquid has a higher boiling-point than 50–60° C., as water has, we use heat from a steam-bath or Bunsen flame to promote the evaporation. In evaporation we allow the vapor of the liquid to escape, because it is the less volatile, dissolved body that we wish to examine. When we desire, on the contrary, to examine the liquid, the vapor

must be condensed. This method, which we have not yet had occasion to employ, is called **distillation** (Fig. 16). The jacket round the long tube is filled with a stream of cold water, which, on account of its high specific heat, quickly cools and condenses the vapor. The resulting liquid is caught in a flask.

These methods may be adapted to the investigation of any similar problem. Thus, gunpowder is made by the intimate mixing of sulphur, charcoal, and saltpeter (potassium nitrate). If no chemical interaction whatever has occurred, a sample will be wholly separable into these components. If a partial change has taken place, a certain amount of

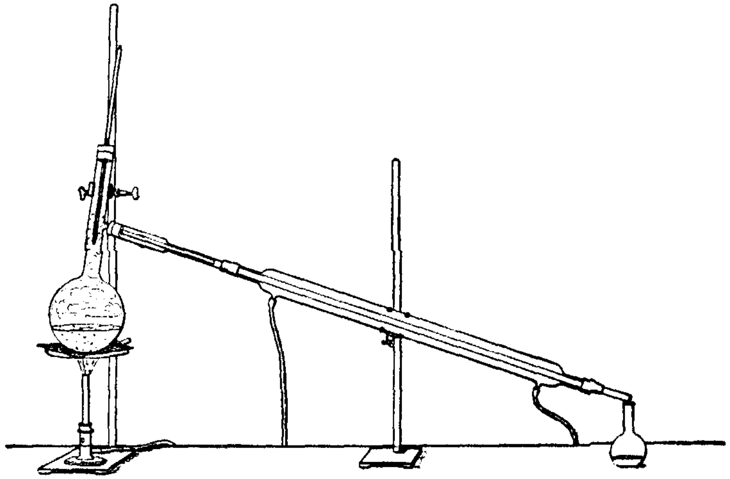


FIG. 16.

material with different properties will be discovered in the mixtur If the change has been complete, no portion of the original substanc will be found. We must first study the specific properties of each the ingredients separately, in order that a plan of separation may devised, and that we may have a basis for comparison with the products of the separation.

The experiments with mercuric oxide (p. 12) and with silver nitrate (p. 13) simply ring the changes on the same conceptions. When we heat the former it is resolved into its constituents. We selected the experiment because the conditions are such that separation of the products from each other and from the original material occurs spontaneously without further manipulation. The separation depends

here on the boiling-points of the materials. That of oxygen is very low (−183° C.); so that, being a gas even at ordinary temperatures, it comes off. That of mercury is much higher (357° C.), but the heat produced by the flame (1000°–1200° C. in the bottom of the test-tube) is more than sufficient to vaporize this product also. The speedy condensation on the cooler part of the tube, causing *separation* of the two products, is due to the wide *difference in boiling-points*. The part of the mercuric oxide which is still unchanged, on the other hand, is entirely involatile even at 1200° C.; so that it does not mingle with the vaporized products at all.

In the action of silver nitrate on sodium chloride (p. 13), it was solubility that furnished the means of separating the products. The silver chloride is practically insoluble in water, while sodium nitrate is very soluble. To recover the latter, the boiling-points were then considered, and the more easily vaporized water was driven off.

When, following the latter experiment, the silver chloride was exposed to light, resolution into silver and chlorine took place. The products became separated spatially at once, because chlorine is a gas (substance of low b.-p.) and silver is a solid (usually a substance of high b.-p.).

In every case the specific properties — color, crystalline form, and so forth — by which recognition is effected were mentioned.

In connection with the foregoing, the following points should be noted:

1. That coincidence in *two* or *three* specific properties is generally sufficient to establish identity.

2. That we usually have to *separate* the components of a mixture or solution before identification can be effected.

3. That if our problem were the *making* of a particular compound whose constituents were known, we should study the products of each attempt by the above method. Our object being to get the compound as a pure substance, we should try to arrange the composition of each of the initial substances (apart from the necessary constituent) so that any by-products formed should have such properties that we could readily effect a separation of them from the desired compound.

4. That a wide knowledge of specific physical properties is required for intelligent chemical work (*cf.* pp. 36–39 and 65).

5. That our methods are purposely limited so as not to separate chemically combined, but only physically mixed, forms of matter: *after* a physical individual has been isolated, and even then only if it has new

properties, and is not recognized as a known substance, we next proceed to separate it into its chemical constituents so as to learn which constituents it contains and in what relative proportions by weight.

Summary. — In this chapter we have added considerably to our conception of the scope of chemistry (*cf.* p. 16). Although our survey is by no means yet complete, we may condense our results as follows:

Chemistry deals with the changes in composition and constitution which substances undergo and with the transformations of energy which accompany them. To convert the isolated facts into a science we classify related parts under laws, such as those of conservation of mass (p. 17) and of energy (p. 23), and under conceptions, such as those of chemical energy (p. 25), element (p. 31), body (p. 34), substance (pp. 26, 32, and 35). We also distinguish between attributes, specific properties, and conditions (pp. 35–36). In the last paragraphs we have indicated briefly the use to which these conceptions and this classification are put.

Chemical laboratory work consists largely in the separation, recognition, and description of substances. The importance, especially, of thorough familiarity with specific properties and the influence of conditions (for example, temperature) to these ends is shown by the examples (pp. 36–39). The system of classification as a whole is part of the everyday mode of thought of the chemist, for thought consists largely in comparing and contrasting, and our system of classification furnishes the norm of this so far as chemistry is concerned. Learning chemistry consists, therefore, in learning this classification and becoming habituated to its use.

The influence of conditions has as yet been barely touched. It will be dealt with more explicitly as occasion offers. The attribute of quantity, which has already received some attention (pp. 8, 17), will form the basis of discussion in the next chapter.

Exercises. — 1. Define the following terms, and find illustrations of each, other than those given on pp. 34–39: mixture, physical component, chemical constituent.

2. Describe (*a*) a red-hot rod of iron, (*b*) an aqueous solution of sugar, employing all the terms given on pp. 34–36 so far as they are applicable.

CHAPTER III

INTRODUCTORY III

The Law of Definite Proportions, Sixth Characteristic of Chemical Phenomena. — In making a chemical compound, may we use varying proportions of the constituents? The controversy between Berthollet and Proust, in which the former supported the affirmative and the latter the negative side of this question, was one of the chief features of the chemical history of the early part of the nineteenth century. The ways of forming or decomposing a compound, or of carrying out a more complex chemical change, may be varied indefinitely. The apparatus, the mode of experiment, and the proportions of the materials, may be altered at our will. But, in spite of an enormous amount of careful work, no case of variation in the proportion of the constituents *actually used* or *produced* in a given chemical action has come to light. If too much of one constituent, for example, is taken, a part simply remains unchanged. A higher temperature may hasten the chemical action, but it does not affect the quantitative composition of the products, provided the resulting substances are of the same nature. It was the work of Stas (1860–65) which settled the question by proving that even slight variations cannot be detected. It is, therefore, a characteristic of chemical phenomena that: **In every sample of each compound substance formed or decomposed, the proportion by weight of the constituents is always the same.** This statement of fact is known as the **law of definite proportions.** When the composition of a substance seems to be variable, it is always found on closer examination that mechanical mixtures of some kind were being mistaken for pure substances.

Another form of statement, which is a corollary of this one, and is applicable more directly to complex chemical actions, is: The ratio by weight of any one of the factors or products of a chemical change to any other is constant.

The Law of Multiple Proportions, Seventh Characteristic. — In the course of even a very limited experience in the examination of chemical compounds, we should be bound to find that among the substances which we examined were cases of two or more perfectly dis-

tinct bodies, made of the same elements, but on analysis found to contain different proportions of the constituents. We should discover that each of those distinct substances had a constant composition peculiar to itself. Thus, we find in nature a beautiful yellow mineral known as pyrite. A pure sample of this contains nothing but iron and sulphur, and yet the composition of the substance is entirely different from that of ferrous sulphide (p. 12). The percentage of the constituents in each is as follows:

	Ferrous sulphide.	Pyrite.
Iron	63.59	46.62
Sulphur	36.41	53.38

If we calculate from these data how much of one of the elements is combined with identical amounts of the other in each of the two compounds, a simple relation emerges from the seemingly unrelated proportions. Thus, taking one part of iron in each, we find $63.59 : 36.41 :: 1 : x$ ($= 0.5725$) and $46.62 : 53.38 :: 1 : x$ ($= 1.145$). Thus the quantities of sulphur (0.5725 and 1.145) combined with one part of iron, in ferrous sulphide and pyrite respectively, are in the ratio 1 : 2. The reader will find by calculation that if the quantity of sulphur, instead of that of iron, be fixed at any value, the proportions of iron in the compounds will then stand in the ratio 2 : 1.

Again, sulphur burns in the air, forming with oxygen a gaseous substance whose odor is familiar. But a different compound of the two elements, generally seen in the form of a white fibrous solid, is much used in dye-factories. In the former, the proportion of sulphur to oxygen is almost exactly 1 : 1 (50 per cent of each), while in the latter it is 1 : 1½ (40 per cent sulphur and 60 per cent oxygen). Thus the two different proportions of oxygen combining with one part of sulphur are in the ratio 1 : 1½ or 2 : 3.

The existence of this simple relation is not an accident, and confined to these cases. It is a rule to which no exception has yet been found. More complex examples yield the same result.

Thus there are known over two hundred compounds of carbon and hydrogen, all different in composition. But if we fix the quantity of one of the elements and find the amount of the other which, in each compound, is combined with that quantity, the ratio of these amounts to each other is expressible by integral numbers. Take, as a sample, the compositions of four of these substances: methane, acetylene, ethylene, and naphthalene (moth-balls) contain respectively 3, 12, 6, and 15 parts of carbon combined with one part of hydrogen.

These ratios are not those of *approximately* whole numbers. The more carefully our determinations of the proportions of the constitu-

ents in the several compounds have been made, the more *exactly* do *integral* numbers represent the numerical relations between the results.

This principle was discovered by Dalton (1804), and was embodied by him in a statement known as the **law of multiple proportions**, which ran somewhat as follows: **If two elements unite in more than one proportion forming two or more compounds, the quantities of one of the elements, which in the different compounds are united with identical amounts of the other, stand to one another in the ratio of integral numbers, which are usually small.**

The Measurement of Combining Proportions. — The most *exact* measurement of the proportions in which the elements combine to form compounds involves manipulations too elaborate to be gone into here. Operations of the same nature are described in works on quantitative analysis. One or two brief statements, diagrammatic rather than accurate, will show the principles, however.

If we take a weighed quantity of iron in a test-tube and heat it with more than enough sulphur (an **excess** of sulphur), we get free sulphur along with the ferrous sulphide (p. 12), and no free iron survives. We may remove the free sulphur by washing the solid with carbon disulphide. The difference between the weights of ferrous sulphide and iron gives the amount of sulphur combined with the known quantity of the latter.

As an example of the study of rusting, we may weigh a small amount of copper in the form of powder in a porcelain boat and pass oxygen over the heated metal (Fig. 17). The formation of cupric oxide takes place rapidly. If we limit the oxygen, part of the copper may remain unaltered; if we use it freely, the excess will pass on unchanged. A given weight of copper cannot be induced to take up more than a certain amount of oxygen, and use of a less amount simply limits the amount of copper transformed into oxide. The original weight of the copper, and the increase in weight, representing oxygen, give us the data for determining the composition of cupric oxide. The record of the result is usually made in the form of the quantity of each constituent in a hundred parts of the compound, and is called the percentage composition.

The data furnished by one rough lecture-experiment, for example, were as follows:

Weight of boat empty	3.428 g.
Weight of boat + copper	4.278 g.
Difference = weight of copper	0.850 g.

Weight after addition of oxygen	4.488 g.
Weight without oxygen	4.278 g.
Difference = **weight of oxygen**	**0.210** g.

The proportion of copper to oxygen, so far as this one measurement goes, is therefore 85 : 21.

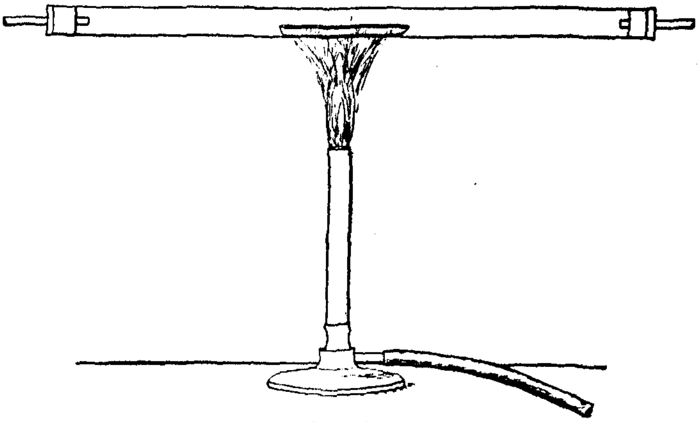


FIG. 17.

To find the percentage of each constituent, we observe that the proportion of copper is 85 : 85 + 21, or $\frac{85}{106}$ of the whole. That of the oxygen is $\frac{21}{106}$ of the whole. Thus the percentages are:

Copper,	$106 : 85 :: 100 : x$	$x = 80.2$
Oxygen,	$106 : 21 :: 100 : x'$	$x' = 19.8$

Naturally, the mean of the results of a number of more carefully managed experiments will be nearer the true proportion. The percentages at present accepted as most accurate are 79.9 and 20.1.

In the case of mercuric oxide, we may decompose a known weight of the oxide (p. 12) and afterwards weigh the mercury and ascertain the oxygen by difference.

Finally, a strip of the metal magnesium may be set on fire in the air. It gives out a dazzling white light in burning, and on this account the powdered metal is used in making flash-light powder for photography. The product is magnesium oxide, a white substance, which partly rises as a dense smoke and partly falls on the ground. In a loosely closed porcelain vessel (Fig. 18) the metal may be burned slowly, with the help of the heat from a small flame, and the oxide may be retained.

The weight of magnesium ribbon taken and the increase in weight due to oxygen give the data for calculating the proportions of the constituents.

The following figures show the results of experiments in these and other simple cases, and represent the percentage composition of the products, only two places of decimals being given in each case. They will be required for the discussion of the next topic.

(1) Cupric oxide		(4) Cupric sulphide		(7) Cupric chloride	
Copper,	79.9	Copper,	66.48	Copper,	47.3
Oxygen,	20.1	Sulphur,	33.51	Chlorine,	52.7
(2) Mercuric oxide		(5) Mercuric sulphide		(8) Mercuric chloride	
Mercury,	92.59	Mercury,	86.18	Mercury,	73.8
Oxygen,	7.41	Sulphur,	13.81	Chlorine,	26.2
(3) Water		(6) Hydrogen sulphide		(9) Hydrogen chloride	
Hydrogen,	11.18	Hydrogen,	5.92	Hydrogen,	2.76
Oxygen,	88.81	Sulphur,	94.07	Chlorine,	97.23

The Law of Combining Weights, Eighth Characteristic. — The ratios in the above list represent the true proportions by weight in the various compounds, but naturally the individual numbers constituting those proportions have no chemical significance whatever. They are arbitrary, values selected so that the constituents of the proportion may together make 100. Each pair represents the constant ratio which is the mean result of numerous experiments.

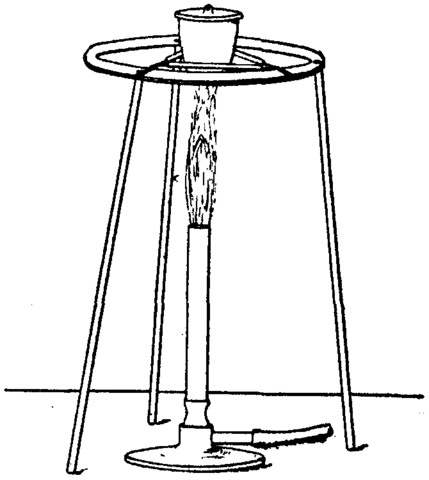


FIG. 18.

We begin the effort to reduce these numbers to order by selecting one element as our starting-point, and by taking some convenient weight of it as the basis. As we shall see, it makes *no difference* what choice we make in either respect. To avoid waste of time, we shall, therefore, use oxygen, as it is the element generally preferred by chemists for the purpose. The reason for this preference will be apparent later (see pp. 48, 51)

We should naturally be inclined to use 1 part of the element as our basis. But our later steps involve finding out what amounts of the other elements combine with this quantity, and we perceive that the amount in the case of hydrogen will be only 0.126 parts. We calculate this from (3): 88.81 : 11.18 : 1 : x (= 0.126). If, however, we take 8 parts of oxygen, this amount of hydrogen is also increased eight times and becomes 1.008. As no element is found to combine in smaller proportions than hydrogen, we are satisfied that a scale for our numbers based on 8 parts of oxygen will not involve any values less than 1. The choice of scale is purely one of convenience.

Our further procedure is determined by a desire to demonstrate a particular relationship, and so we must keep a fixed principle in mind. This principle is that of calculating a series of combining proportions of which each succeeding member is the amount of some element which combines with the amount of the one preceding it in the list. Oxygen is the initial member of the series.

From (1) we calculate the amount of copper combined with 8 parts of oxygen, thus: 20.1 : 79.9 : : 8 : x (= 31.8). We next look for an element which combines with copper — any such, whether it appeared in the above list or not, would do — and from (4), for example, find, by the same method of calculation, that 31.8 parts of copper unite with 16.03 parts of sulphur. Then we select any element that combines in turn with sulphur, and from (5) learn that 16.03 parts of sulphur unite with 100 parts of mercury. Next we observe from (8) that 100 parts of mercury combine with 35.45 parts of chlorine. Finally, from (9) we calculate that 35.45 parts of chlorine unite with 1.008 parts of hydrogen. Setting these results down in order, we obtain the series:

Oxygen	Copper	Sulphur	Mercury	Chlorine	Hydrogen
8	31.8	16.03	100	35.45	1.008

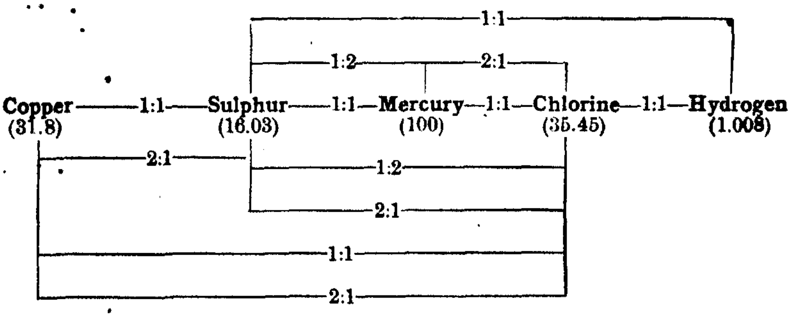
Since each of these numbers represents the amount of the corresponding element which is actually found to *combine* completely with the quantities of two other elements, we may call them **combining weights**. It must be observed, however, that those of our measurements of which we have made use in deriving them relate each number in the series to its *two immediate neighbors only.*

Now (2) gives the proportion in which oxygen combines with mercury. By calculation, 7.41 : 92.59 : : 8 : x (= 100), we find that 8 parts of oxygen combine with 100 parts of mercury. It must be pointed out explicitly that this result for mercury and oxygen is en-

tirely independent of the previous one for mercury and sulphur, by which the value 100 was originally derived. It is based upon the independent measurement of the proportion of mercury in mercuric oxide, and *we could not possibly have foretold what this proportion would be.* It appears then that the above combining weights, at first measured for neighboring pairs only, are also the weights according to which remoter combinations take place. Further study confirms this speculation. Thus (3) shows that oxygen and hydrogen combine in the proportion 8 : 1.008, and (7) gives the proportion in cupric chloride, and (6) that in hydrogen sulphide exactly as they stand in the series.

A few other pairs in this set are capable of uniting. For example, oxygen and sulphur, as we have seen, form two compounds in which the proportions are found to be 2 × 8 : 16.03 and 3 × 8 : 16.03. Sulphur and chlorine unite in the proportions 16.03 : 2 × 35.45 and 2 × 16.03 : 35.45. Sulphur and copper form another compound, cuprous sulphide, and in it the proportion is 16.03 : 2 × 31.8, instead of 16.03 : 31.8. These examples are also, incidentally, illustrations of the law of multiple proportions (p. 43).

These relations become clearer when represented diagrammatically. Thus the five elements, omitting oxygen, give the following compounds and no others:



It will be observed that hydrogen forms stable compounds with only two of the other four elements in the series. If, however, oxygen had been included, compounds of oxygen with all the other five would have demanded recognition. This illustrates the reason given below for the preference of oxygen as the fundamental element.

It ought to be added that combinations of three or more elements are not uncommon, but neither does examination of these cases reveal anything in conflict with the principle which our study of the combining weights is bringing to light. For example, oxygen, chlorine, and hydrogen combine in the proportions:

2 × 8 : 35.45 : 1.008, 6 × 8 : 35.45 : 1.008, and 8 × 8 : 35.45 : 1.008.

A complete study of all known combinations of all the elements shows that *no compound* containing any two or more of the elements *is known, whose composition cannot be expressed in terms of the combining weights* found in a series like the above, by using proper integral factors when necessary.

This statement would remain true whatever element we chose as the initial one of the series (see Exercise 1, p. 52), whatever combining weight we assigned to that element, — for this affects only the scale of all the members, not their relative values, — and whatever the order in which the succeeding elements were taken. It applies to all the elements without exception, for the above series might have been extended to include all the known elements. It represents, in fact, not a property of our method of manipulation, but of chemical combination itself.

It will now be seen that, since the order is a matter of indifference, a long series like the above is not needed, and would lead only to cumulative errors. The exact determinations of the combining weights of most of the elements have actually been made by direct union with oxygen or with the help of but one intermediate step. Again, if the question had been one of mathematics, hydrogen, the element with the lowest combining proportions, would have furnished the basis and unit of the scale. But the question was the practical one of getting the most accurate measurements for the relative magnitudes of the numbers, so oxygen was chosen instead. Nevertheless, the value 8 was selected in order that the advantage of having a mathematical unit, or something close to it, in the combining weight of hydrogen, might be retained also.

The law of combining weights may be put briefly thus: **The proportions by weight in which all chemical combinations take place can be expressed in terms of small integral multiples of fixed numbers called combining weights, one for each element.** It describes what is perhaps the most striking of all the characteristics of chemical action.

It is, perhaps, hardly necessary to point out that the laws of definite and multiple proportions are simply partial statements whose whole content is included in this far greater generalization. No one chemist succeeded in discovering this property of combining weights. The work of J. B. Richter, Dalton, and many others contributed to it.

Without this fact, the remembering of the compositions of chemical substances, necessary as it is to the chemist, would have been completely beyond the power of any ordinary memory. With it, the task becomes comparatively simple. It is only necessary to decide on the best system of values for the combining weights, and then, *regarding*

the value of this for each element as the unit of weight for that element, to express the proportions of the element in every compound by the proper multiples. Thus, given a list of the combining weights, one for each element, only the small integral multiples have to be kept in mind in connection with each compound.

The reader will require a little time, however, before he becomes accustomed to the use, not of a single unit of weight, but of a different one for each element. Chemistry is the only science in which the physical unit of weight, which is the same for all materials, is not employed for every purpose. The physical manipulations of the chemist are carried out with the use of physical units, but the chemical results are expressed in terms of individual unit quantities of the several elements, the combining weights.

The individual units actually used for each element are not in all cases identical with those we have given. The final values will be discussed in the next section but one.

Most of the first exact determinations of combining proportions were made by Berzelius before 1830. It should be added that, while the combining weights, with the exception of that of oxygen which is the standard, are never actually whole numbers, although they often approach such integral values, the integers used to multiply them, when they are employed to express combining proportions, are so most exactly. Even in determinations by methods of the highest refinement, the factors to be used in multiplying the combining weights are always found to diverge from whole numbers by amounts within the known errors of the method of measurement.

Equivalents. — The combining weights may be viewed from another standpoint. The relation between the first three members of the series discussed in the last section, for example, may be stated thus: 16.03 parts of sulphur and 8 parts of oxygen combine with identical amounts of copper, namely, 31.8 parts. Either of them will satisfy the same amount of this third element. In fact, they are **equivalent** for the purpose of combination. Similarly, 31.8 parts of copper and 100 parts of mercury are equivalent, because either will hold 16.03 parts of sulphur in combination.

Now, copper will actually displace mercury from combination with a third element. The copper will combine with the third element, and the mercury will be set free. So, if we know the combining weight of copper, but not that of mercury, we can make a measurement of the amount of mercury displaced by 31.8 parts of copper. This amount (100 parts), which we then call the "equivalent," will be also the re-

quired combining weight. It will be so because this amount of mercury was formerly in combination with that quantity of the third element with which 31.8 parts of copper are now united. The terms combining weight and equivalent both refer to the *same* members, and the latter simply emphasizes a particular experimental method. Following the custom of chemists, we shall hereafter refer to the combining weight on the scale oxygen = 8 as the equivalent of the element. The **equivalent weight** of an element **is the quantity of the element which combines with or displaces 8 parts of oxygen or 1.008 parts of hydrogen.**

Atomic Weights. — The chemist frequently uses the idea of equivalents and the values we have given them. But far more often he employs a slightly differing set of numbers, which, for reasons that will appear in a subsequent chapter, he calls **atomic weights.** The following list shows the elements whose equivalents we have been discussing, along with one or two others, added by way of furnishing a fair sample, and gives both sets of weights for the purpose of comparison:

Element.	Equivalents (Combining Weights).	Atomic Weights.	Element.	Equivalents (Combining Weights).	Atomic Weights.
Oxygen . . .	8	16	Iron	27.95	55.9
Copper . . .	31.8	63.6	Magnesium .	12.18	24.36
Sulphur . .	16.03	32.06	Carbon . . .	3.00	12.00
Mercury . .	100.0	200.0	Aluminium .	9.03	27.1
Chlorine . .	35.45	35.45	Sodium . . .	23.05	23.05
Hydrogen . .	1.008	1.008	Bromine . .	79.96	79.96

It will be seen that some equivalents have been multiplied by two, the first four and those of iron and magnesium, for example; some have been multiplied by three, like that of aluminium; some by four, like that of carbon; and some remain unchanged, like those of chlorine, hydrogen, sodium, and bromine.

The reasons for this manipulation of the simple equivalents found by experiment is based upon theoretical considerations. As it is impossible, until we reach certain important facts which cannot be introduced here, to explain these considerations, the discussion of the reasons for the changing of the numbers will be postponed until after these facts are before us. Suffice it to say that great advantages are found to attach to these modifications in the values. The step from equivalents to atomic weights (*q.v.*) is taken before the justification of

it can be given, because otherwise formulæ (see next chapter) could not be used in the earlier chapters, and so the advantages their employment offers would be sacrificed.

A little thought will show that the atomic weights have all the properties which we have shown to belong to the combining weights (equivalents). The atomic weight is the unit of weight (p. 49) actually used in expressing the proportions of each element in all its compounds. The integral factors are, of course, different from those which would be employed in expressing the composition of the same substance in terms of equivalents, because many of the latter have been multiplied by small integers already in course of being made into atomic weights. But the multiplication has in every case been by an integer, so that no change in the properties of the numbers has occurred.

To the reasons given above for the choice of oxygen as the fundamental element, and the value 8 for its combining or equivalent weight, one other may now be added. The majority of the atomic weights, calculated on this basis from the experimental results, fall so close to being integers that the nearest round numbers are exact enough for ordinary use. Thus in the above list nine of the twelve atomic weights are within 0.1 of the nearest whole number. This convenience disappears when, for example, hydrogen with the value 1 is made the basis.

The reader will inevitably find difficulty at first in thoroughly grasping the significance of these numbers. It may, therefore, be of some assistance if a hint is thrown out which will suggest a concrete basis for this curious property. These numbers appear to mean that, when we wish to make a chemical compound, we may choose any two elements from the list, and, if it is found that they can combine at all, we have only to take the atomic weights, worked out from other combinations of each element, and we shall find that they will exactly suffice for this case of chemical union. If *complete* combination of both materials does not take place, then trial will quickly show what multiples of the atomic weights will result in this. The situation seems to suggest that the constructing of chemical compounds depends upon the putting together of ready-made "parts," like those of a watch or a bicycle. The parts seem to be "interchangeable," and each element seems to be furnished to us by nature in ready-made packets suitable for application in building up any chemical structure.

A complete list of atomic weights is printed on the inside of the cover at the back of this book.

Summary. — This chapter adds an important item to our statement of the scope of the science (*cf.* p. 40), which, therefore, now reads as follows: Chemistry deals with the *quantitative* study of the changes in composition and constitution which substances undergo and with the transformations of energy which accompany them. To express the quantitative relations which are observed, a different unit of weight is employed for each element, and is known as the atomic weight of the element.

There are other important characteristics of chemical phenomena mostly concerned with the conditions (p. 35), but those which have been given are sufficient, for the present, to guide us in the systematic study of the behavior of the elements and their chief compounds.

It may not be out of place to indicate which are the most important conditions. The first condition whose influence we are likely to notice in chemical work is that of *temperature*. The accelerating effect of rise in temperature on the speed of all chemical changes (see Chap. v), and van 't Hoff's law (*q.v.*) in regard to the effect of temperature on the direction of chemical change, describe the most important characteristics of this influence.

The second condition whose effects we continually observe is that of *concentration*. This, and not chemical affinity, as many suppose, determines chemical behavior in the majority of familiar actions. It is described by the law of concentration (*q.v.*), or "mass action," as it is often inappropriately called to the great detriment of clearness. Brin's method of obtaining oxygen furnishes the first conspicuous case of the influence of this condition which we shall encounter. If this and many other examples are passed over without discussion, it is only because we must wait until much chemical experience has been gained before this principle can be understood. *Pressure* is the special name for concentration in gases.

A third condition of great importance in many — perhaps most — chemical actions is the presence of a *catalytic agent* (*q.v.*).

Exercises. — 1. Starting with mercury as the basal element and 100 as its combining weight, calculate from the data on p. 45 a series of combining weights for the other five elements. Then show that this series has the same properties as that discussed in the text.

2. There is another oxide of copper, namely, cuprous oxide, which differs in properties and composition from cupric oxide. In it the ratio of copper to oxygen is $2 \times 31.8 : 8$. If this compound had been used in deriving the combining weight of copper on p. 46, what effect would this procedure have had on the rest of the series? Would the properties of the series have been affected?

3. Calculate the equivalent (combining) weight of iron from the composition of ferrous sulphide (p. 42).

CHAPTER IV

INTRODUCTORY IV

A CONSIDERATION of the contents of the foregoing chapter will show that the complete description of a chemical change must be exceedingly involved. In a moderately complex action, such as that of sodium chloride upon silver nitrate, we should say that sodium chloride, composed of one atomic weight each of sodium and chlorine, when brought in contact with silver nitrate, composed of one atomic weight each of silver and nitrogen and three atomic weights of oxygen, *gave* silver chloride, composed of one atomic weight each of silver and chlorine, and sodium nitrate, composed of one atomic weight each of sodium and nitrogen and three atomic weights of oxygen. Such a statement, while it would give all the facts from the quantitative point of view, would be difficult to grasp and lacking in perspicuity.

Symbols, Formulæ, and Equations. — In order to represent the nature of a chemical change in a form which may be taken in at a glance, the chemist is in the habit of using certain **symbols**, first introduced by Berzelius. Thus, the letters Ag represent one atomic weight (*i.e.*, 107.93 parts) of silver (*argentum*), and O represents one atomic weight (*i.e.*, 16 parts) of oxygen. In other words, the symbol of an element means one chemical unit weight of the element. Since many elements begin with the same initial, two letters have frequently to be used to distinguish them. When the names of the elements are not the same in all languages, resort is frequently had to Latin. Thus, Cu stands for one combining weight of copper (*cuprum*), Fe is used for iron (*ferrum*), Hg for mercury (*hydrargyrum*). From German we have Na for sodium (*natrium*) and K for potassium (*kalium*). To represent a compound, the symbols of the elements which it contains are placed side by side, small numbers indicating multiples of the atomic weights where they occur. Thus, sodium chloride is represented by the symbols NaCl, silver nitrate by the symbols $AgNO_3$. A combination of symbols is called a **formula**. The symbols of a formula, taken by themselves, do not stand for any definite quantity; each is one

factor of a proportion. Ag means the proportion of 107.93 parts of silver to the proportions of the other elements represented by the other symbols which may be connected with it.

The value of these symbols lies not only in the compact way in which the resulting formulæ present the composition of compounds, but also in the use which may be made of them in showing at a glance the details of a chemical change. The chemical action just mentioned appears as follows:

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3.$$

This expression contains all that was conveyed by the words which were written out in full above. The arrow indicates that the materials on the left-hand side pass, in the chemical transformation, into those on the right-hand side. Such symbolic expressions are called **equations**.

One other variation is in frequent use. If we could make pyrite (p. 42) by the union of iron and sulphur, we should require two atomic weights of the latter to one of the former. The equation would run thus:

$$Fe + 2S \rightarrow FeS_2.$$

It will be observed that we employ the form 2S before combination and S_2 (in FeS_2) after it. The reasons for this usage will become clear as we proceed. We note simply that 2S means 2 separate atomic weights of sulphur, as $3FeS_2$ would mean three separate **formula-weights** of pyrite. The same *substance* (*cf.* p. 32), sulphur, might appear as 5S or 8S in other equations, according to the proportion needed. But FeS_2 is a group of three atomic weights united chemically. The *substance pyrite* never contains anything but two atomic weights of the *element* sulphur, and its formula is invariable. Thus the *regular* integers multiplying the atomic weights in the composition of a particular compound are written *after* the symbols of the elements, while more arbitrary factors which change from one use of the substance to another are written in front.

We shall find later that there are two substances containing nothing but oxygen, and that each is a compound of the element with itself. The molecular formulæ of these two are O_2 (oxygen) and O_3 (ozone). Thus O or 2O or 3O would all be used for different proportions of the substance O, if such a *substance* were known, and O would be used for a substance made of oxygen, but different from oxygen or ozone. Molecular formulæ will not be employed here until after Avogadro's hypothesis has been discussed. They will then be used exclusively.

The object in writing a series of formulæ in the above manner is to show

that the system upon the left-hand side, consisting of certain substances whose composition and properties we know, is, under the conditions of the experiment, unstable, and changes into the system upon the right-hand side, whose nature we also know. The materials on the two sides are essentially different, for the transformation represented is a chemical *change*. It is somewhat anomalous, therefore, that, to connect two sets of things which are essentially different, the sign = is usually employed. To call this a *chemical* equation is still more anomalous, since it is precisely in the chemical point of view that the difference between the two sides is most strongly to be emphasized. It represents two sets of things which are different and not alike chemically. The physical properties of the two sets of substances are likewise totally unlike. There is only one respect in which the materials on the two sides agree, and that is that their mass is not different. This is, however, merely an example of the law of conservation of matter, and need not, therefore, be specially commemorated in the form in which we write every equation. It may be assumed that the equality in mass holds for all chemical changes until some case where it does not hold shall have been discovered. Above all it must be remembered that the chemical equation is not an algebraic expression; it is subject to none of the rules of algebra. It is a brief expression, in terms of the combining weights, of the distribution in kind and quantity of the constituents of a system before and after chemical change.

Making Formulæ and Equations. — The making of a chemical equation, it is needless to say, involves (1) a knowledge of the proportion of the constituents in each compound used and produced. These are ascertained by experiment, and are at first stated in ordinary physical units of weight. We require (2) a knowledge of the chemical unit weights — the atomic weights — which have been accepted by chemists for each element concerned, since the proportion is to be expressed in terms of the chemical units of weight proper to each element. By factoring the terms of the first proportion so that one factor in each case is the atomic weight, we discover whether multiples of the atomic weights will be required to represent the composition of the substance, and if so what these must be. We may then introduce the symbols in place of the atomic weights, and construct the formula for each compound. It is necessary (3) to know the proportions in which the various compounds concerned are used and produced. These give us the multiples of each formula as a whole, and we are then in possession of everything required to make the equation.

It will be seen that not all of these facts are independent of one another, so that a complete measurement of everything is not in practice required. Thus, knowing the total number of atomic weights of oxygen used on the left-hand side of an equation, we see from the laws of the conservation of mass and matter that this number must appear on the other. So that if, for example, but two products are

formed, and only one of them contains oxygen, we obtain by inference some definite information about the composition of this substance. In other words, in obtaining the complete information needed in making equations, we may frequently reduce the actual work of measurement, and reason out the minimum number of proportions that must be measured, by a careful study of the nature of each change. Then, use of the law just mentioned and of our general knowledge of the nature of the action will enable us to complete the equation. It will be seen at once that since we have no means of knowing *a priori* what the proportions in the resulting compound will be, if we make an experiment with unmeasured quantities of the substances, we must lack the data for making the formula. It is, therefore, absolutely impossible to construct a chemical equation unless we have obtained by experiment and by inference all the information required under the heads enumerated above. Placing the symbols of the elements side by side, for example, does not suffice, since we do not know what multiples of the atomic weights may be involved.

Let us take an actual illustration which will make all this clear. Suppose the problem is to make the formula of dried rust and the equation representing its production from iron, and that very refined experimental methods are not used. By weighing before and after the change we get the weight of the iron and of the corresponding amount of oxygen in the rust it produces. If we took 2 g. of iron we should get about 2.86 g. of rust. So that the proportion of iron to oxygen is $\frac{2}{0.86}$. The atomic weights are 55.9 and 16 respectively. Since these have been selected so as to conform to the law of combining weights (p. 48), this proportion must be expressible in the form $\frac{x \times 55.9}{y \times 16.0}$, in which $\frac{x}{y}$ is a ratio of two small integers. To find the value of this ratio we have,

$$\frac{x \times 55.9}{y \times 16.0} = \frac{2}{0.86},$$

from which,
$$\frac{x}{y} = \frac{2 \times 16.0}{0.86 \times 55.9} = 0.65, \text{ or about } \frac{2}{3}.$$

Substituting these values for x and y, and the symbols for the atomic weights, the proportion appears as $\frac{2 \times \text{Fe}}{3 \times \text{O}}$, and the formula of the

compound is Fe_2O_3. We perceive at once that the equation must be,

$$2Fe + 3O \rightarrow Fe_2O_3,$$

since we must take enough material to make the product. In this case one measurement (the ratio of iron to rust), the knowledge of the atomic weights (which, of course, depend upon the experimental work of chemists), and the law of conservation of mass, constitute the necessary and sufficient equipment for learning all about the change quantitatively, and, therefore, for making the equation.

When more than two constituents make up a compound, the same principle is used. Thus, if we find a substance containing 27.09 per cent of sodium, 16.50 per cent of nitrogen, and 56.41 per cent of oxygen, we resolve each percentage into the desired factors by dividing it by the corresponding atomic weight. This gives us:

	Percentage		At. Wt. Factor		Using Symbols	÷ 1.175
Sodium,	27.09	=	23.05 × 1.175	or	Na × 1.175	Na × 1
Nitrogen,	16.50	=	14.04 × 1.175	or	N × 1.175	N × 1
Oxygen,	56.41	=	16.00 × 3.526	or	O × 3.526	O × 3

Now the composition of all known compounds can be expressed by *integral* multiples of the atomic weights. We must, therefore, find the whole numbers which stand in the same ratio as the three fractional factors. We may divide all the factors by 1.175, since the composition of the compound is a question of ratio simply. This gives the integral numbers 1, 1, and 3, and the formula $NaNO_3$.

It is hardly necessary to add that a chemical equation gives the proportions of the materials and nothing more. The physical conditions, for example, whether the substances are dissolved in a liquid, or are in the state of gas, or are at a high temperature, have no place in it. Yet it is absolutely necessary that these facts should be known also. The physical properties of the substances concerned, and also the energy in the form of heat or electricity which may appear or disappear in the process, are likewise left entirely out. A question in regard to the nature of a particular chemical change demands in answer a full statement of all these things. The equation is therefore an essential part, but only a part, of such a statement.

That the formulæ and equations can deal only with the *material* part of the substances undergoing change, and not with their energy (p. 26), is shown by a moment's consideration. Consistency is to be secured only by holding that the symbol S, whether alone or combined with others, stands for the matter-part of the sulphur (for the element, in fact, see p. 32). It is 32 parts by weight of sulphur-

matter. Only in this way does it preserve the same significance on both sides of the equation $S + O_2 \longrightarrow SO_2$. If S on the left side stood for the *free substance sulphur*, then it would stand for 32 parts of sulphur-matter plus the appropriate amount of energy. In this case the S on the right side would have a different signification, and represent a less amount of energy. This is only the beginning of the difficulty, for we then find that S in H_2SO_4 represents the same weight of sulphur-matter with still another proportion of energy, and S has as many interpretations as there are formulæ in which it occurs. Clearly, all references to energy should be rigidly excluded from equations, and thermochemical data can never be given in connection with them without complete sacrifice of consistency. In this book, however, the habit of writing thermochemical equations, being universal, is frequently followed when thermochemical data are given.

Units of Measurement in Chemical Work. — In chemical work temperatures are invariably measured on the Centigrade scale. The temperature of a mixture of ice and water is the zero point. The temperature of the steam which rises from water boiling under a pressure of one atmosphere is represented by 100°. The interval between those two points is divided into one hundred equal parts.

For the expression of length, weight, and volume, the metric system is employed. The unit of this system is the meter, which is subdivided into decimeters, centimeters (cm.), and millimeters (mm.). For small measurements the last subdivision is taken as the unit. A cubic centimeter (c.c.) is the unit of volume for small measurements. For larger ones the liter, which contains 1000 cubic centimeters, is used. The unit of weight is that of one cubic centimeter of water at 4°, the temperature of maximum density. This is called the gram.* For larger amounts of material the kilogram, which contains 1000 grams (1000 g.), is frequently employed. The meter is equal to about $39\frac{1}{3}$ inches in ordinary measures, and the centimeter is very nearly $\frac{2}{5}$ of an inch. One liter is about $\frac{1}{28}$ of a cubic foot and contains 61 cubic inches or 35 fluid ounces. One hundred grams is about $3\frac{1}{2}$ ounces avoirdupois, and one ounce equals 28.35 grams.

Calculations in Chemistry. — In the laboratory it is frequently desirable that we should know what amount of some substance may be obtained by a given chemical action from another, or what amount of material must be used to obtain the desired amount of some product. This information is readily accessible, since measurements of quantity

* In point of fact, the gram is the one-thousandth part of the weight of the standard kilogram kept in Paris. This differs from the weight of 1 c.c. of water at 4° by less than 0.01 per cent.

in connection with most chemical changes are on record. The simplest and most easily handled form of this record is found in the formulæ of compounds, and in the equations representing the changes which they undergo. It is most convenient, therefore, when a question of this kind occurs, to ascertain and write down, first, the equation. Having then before us the information in regard to the quantities in the most condensed form, we may use such parts of this information as are required for the problem in hand.

Suppose, for example, that the question is in regard to the weight of oxygen which may be obtained from 120 g. of mercuric oxide. We write down the equation, and, if the numbers are not familiar to us, we ascertain the atomic weights. These we place then below the symbols by which they are represented, thus:

$$\underset{200+16}{HgO} \rightarrow \underset{200}{Hg} + \underset{16}{O}$$

Reading this equation, it appears that one formula-weight, or 216 parts by weight, of mercuric oxide give one atomic weight, 16 parts, of oxygen, and the question is, What weight of oxygen will be obtained from 120 grams of the oxide? The answer may be stated by simple proportion: $216 : 16 :: 120 : x$, or $16 \times \frac{120}{216} =$ Answer. The reader must conquer a tendency to speak of the symbol O as representing "1 part" of oxygen: it stands for *16 parts.* The word "part" refers to physical units exclusively.

In the very simplest cases it might not seem necessary to write out the equation as a preliminary step, but, wherever the action is more complicated, there will be great danger of errors arising if this is not done. It will be noticed that not all the data which we have written down are necessarily used. In general, only two of the three or more weights which the equation represents will be required. The first thing after writing down the equation is to be sure that the question is brought into relation to the information which the equation gives, and is perfectly understood. Any obscurity on this point is sure to lead to miscalculation.

Exercises. — 1. What weight of sulphur is contained in 100 g. of pyrite?

2. What weight of rust may be obtained with a supply of 10 g. of oxygen?

3. How much silver is contained in 100 g. of an impure specimen of silver chloride which is 33 per cent sand?

4. What are the formulæ of the substances possessing the following percentage compositions?

I		II		III	
Magnesium,	25.57	Sodium,	32.43	Potassium,	26.585
Chlorine,	74.43	Sulphur,	22.55	Chromium,	35.390
		Oxygen,	45.02	Oxygen,	38.025

5. What are the percentage compositions of substances possessing the following formulæ? Mn_3O_4, KBr, $FeSO_4$.

CHAPTER V

OXYGEN

Historical and Introductory. — Almost one-quarter of the atmosphere, by weight, is free oxygen. Water contains nearly 89 per cent of oxygen in combination, and this element constitutes about 50 per cent of common materials like sandstone, limestone, brick, and mortar. On account of its predominance over other elements in quantity, and the exceptional capacity which it exhibits for forming compounds with a great variety of other elements, the systematic study of chemistry may conveniently be begun with oxygen.

While many elements which are less easily obtainable than oxygen have been recognized as distinct substances for many centuries, oxygen did not attain this position until it was first prepared by Priestley in 1774. The reason of this was that gases are not so easy to handle and distinguish as solids or liquids, and consequently very slow progress was made in the study of them. Priestley was particularly interested in examining the nature of the gases which were evolved by some materials when heated. His plan was to fill an elongated glass vessel with mercury (Fig. 19); to invert this in a trough filled with the same metal, and, after allowing the substance under examination to float up into the top of the tube above the mercury, to expose it to the rays of the sun concentrated by a large burning lens. Priestley found that one material, then known as "*mercurius calcinatus per se*" (mercuric oxide), gave off an unusual amount of a gas, or "air" as he called it. He found that this gas supported combustion extremely well and, later, that it was respirable and favorable to the life of small animals, such as mice. He did not, however, recognize that atmospheric

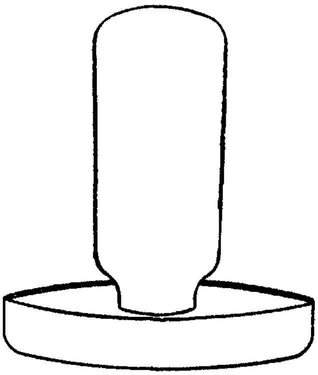


FIG. 19.

air was a mixture, and that the substance he had obtained was in reality identical with that component of the air which has the same properties.

Simultaneously with Priestley's work, Scheele in Sweden had been working in much the same way, and had obtained the same gas from niter, mercuric oxide, and other substances, publication of his results being delayed, however, until 1777.

Meanwhile Lavoisier, in Paris, who had been studying the rusting of metals in the air, heard of Priestley's experiments, and demonstrated that the latter's "good air" was really a constituent of common air, and combined with metals when they formed rusts, or "calces," as they were then called. He proved this conclusively by heating mercury in the retort shown in Fig. 20. The apparatus was arranged in such a way that a definite volume of air was inclosed, within the bell-jar and the retort, by the larger quantity of mercury which filled the trough. During the heating of the mercury in the retort, the familiar red powder (mercuric oxide) was formed on its surface, and simultaneously the volume of air diminished, until after twelve days both of these changes ceased. The air had suffered a shrinkage equal to about one-fifth of its volume, and an easily weighable quantity of the oxide had been obtained. The gas which remained had lost the power of supporting combustion and life, and hence was named by Lavoisier "azote" (Gk. ἀ priv. and ζωή, life). In English it is called nitrogen. The oxide on being heated more strongly by itself gave off a gas whose volume exactly corresponded with the shrinkage undergone by the inclosed air, and this gas possessed in an exaggerated degree the properties which the air had lost. The proof that oxygen was a constituent of the atmosphere was therefore complete. Lavoisier named the new element **oxygen**, or acid-producer (Gk. ὀξύς an acid, γεννᾶν to produce), from the fact that the compounds formed by its union with many elements gave acid (sour-tasting) solutions when they were mixed with water. Cavendish pointed out almost immediately that there were sour-tasting substances which contained no oxygen, so that the name has no longer any significance.

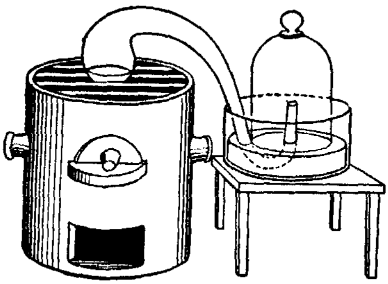


Fig. 20.

Preparation of Simple Substances. — There are two general ways of obtaining simple substances. If the element occurs uncombined in nature, as sulphur and gold do, it is only necessary to free it from foreign materials (impurities) with which it is mixed. If no such supply exists, or if the purification is difficult, then some compound, natural or artificial, is decomposed.

The decomposition, in turn, may be effected in two ways. The compound may be forced apart by the application of energy, usually in the form of heat or electricity, as in Priestley's experiments (*cf.* pp. 19–21). Or the desired constituent may be liberated by offering to the other constituents some substance with which they will unite (see Preparation of hydrogen). When oxygen is to be liberated, the former is the more easily applicable plan.

In selecting our source, we are naturally influenced by the cost of the material, as well as by the ease of the process. Thus, gold oxide yields oxygen by the application of very little heat, but it is extremely expensive. Quicklime is very cheap, but does not give up its oxygen even at the temperature of the electric arc.

Preparation of Oxygen. — 1. Oxygen may be separated from the other substances mixed with it in the atmosphere by liquefying the air (see Liquid air), allowing the nitrogen, which is more volatile, to escape, and finally compressing into tanks the oxygen which evaporates last. This is a purely mechanical process.

2. There are many compounds which, when heated to temperatures under 2000° such as we can obtain with the aid of a Bunsen burner, a coal fire, or a blast-lamp, give up their oxygen. Some of them are minerals, but most of them are manufactured articles. Of the minerals, pyrolusite (manganese dioxide, MnO_2) is an example. It usually contains the elements of water also, and hence moisture is evolved at the same time. A substance identical with the mineral hausmannite (Mn_3O_4) remains. Amongst the artificial sources are mercuric oxide, expensive, but historically interesting (p. 12); barium peroxide, used in manufacturing oxygen on a large scale (Brin's process); and potassium chlorate, the most convenient for laboratory use. Many other substances of this class will be encountered in the sequel.

Brin's Oxygen Process starts from barium oxide (*q.v.*). Barium oxide BaO closely resembles quicklime CaO, but differs from this substance in the fact that when heated in air to about 500°, it rapidly acquires additional oxygen and gives barium peroxide. When barium

peroxide is raised to a yet higher temperature, this extra oxygen is given up again. Barium oxide contains one chemical unit weight each of the two constituents and takes up another of oxygen, so that the equation for the primary action is:

$$BaO + O \rightarrow BaO_2.$$

The subsequent decomposition of the peroxide, during the stage in which the oxygen is made, is the exact opposite: $BaO_2 \rightarrow BaO + O$.* The commercial advantage of the method lies in the fact that the barium oxide remaining after the second stage can be used over and over again. This, as will be seen, is in reality a chemical method of obtaining oxygen from the air.

In practice an improvement on the above principle makes working more economical. It is found that if the barium oxide is maintained at a temperature of 700°, intermediate between the two just mentioned, oxygen is absorbed when air is forced under pressure into the tubes containing the oxide. A valve at the extremity of the tubes permits the escape of the nitrogen. When the combination with oxygen is completed, the pumping apparatus is reversed, and, a partial vacuum being created, the oxygen in combination is given off without any alteration in temperature being necessary. Thus a great waste of fuel is avoided, and the process is rendered more nearly continuous. This method furnishes oxygen about 96 per cent pure, and suitable for sale in compressed form in cylinders.

Potassium Chlorate (*q.v.*) is a white crystalline substance used in large quantities in the manufacture of matches and fireworks. When heated to a moderately high temperature in a tube similar to that in Fig. 5, it gives off a very large volume of oxygen. Examination shows that the whole of the oxygen it contains can be driven out. The white material which remains after the heating is identical with the mineral sylvite. To the chemist it is known as potassium chloride, and, when decomposed, it yields one atomic weight each of potassium and chlorine. Its formula is thus KCl. We may infer, therefore, that the composition of the original substance will be representable by the formula $KClO_x$, where x is the number of atomic weights of oxygen. Measurement and calculation show $x = 3$. The formula is therefore

* In cases where an action is reversible, and the direction depends on conditions which may be altered, we write both equations in one:

$$BaO + O \rightleftarrows BaO_2.$$

$KClO_3$, and the equation for the decomposition (see also under Chlorates):

$$KClO_3 \rightarrow KCl + 3O.$$

To learn the value of x, we ascertain the loss in weight (= oxygen) which a known quantity of potassium chlorate sustains when heated in a hard glass tube closed at one end. By subtraction we get the weight of potassium chloride formerly combined with the oxygen. In an actual experiment, 2.998 g. of potassium chlorate gave 1.169 g. of oxygen and left 1.829 g. of the chloride. The atomic weights of potassium and chlorine are 39.15 and 35.45 respectively, and the formula-weight of the chloride is therefore 74.6. Dividing the measured weights of oxygen and potassium chloride by the corresponding atomic and formula weights (*cf.* p. 57) respectively: $1.169 \div 16 = 0.07306$ and $1.829 \div 74.6 = 0.02452$. We observe that the ratio of the quotients is 2.98 : 1, or almost exactly 3 : 1. The formula is therefore $O \times 3$, $(KCl) \times 1$, or $KClO_3$.

A peculiarity of this action is that admixture of manganese dioxide increases very markedly the speed with which the decomposition of the potassium chlorate takes place. Hence, in its presence, and it is

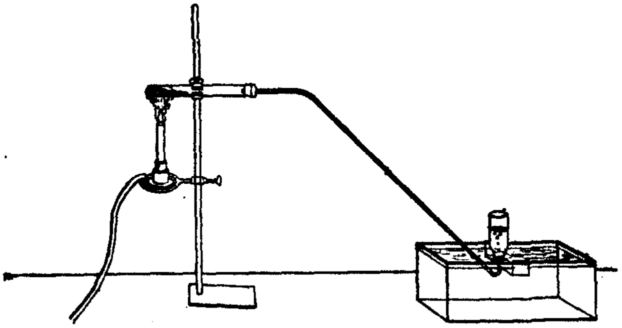


FIG. 21.

generally mixed with the chlorate in laboratory experiments (Fig. 21), a sufficient stream of the gas is obtained at a relatively low temperature (below 200°). Without it no oxygen is evolved at all until the chlorate melts (351°). The dioxide does not begin to lose oxygen below 400°, and therefore is not itself permanently changed in any way when used for this purpose.

Familiarity with Physics Required in the Study of Chemistry. — In mentioning chemical phenomena, it is inevitable that considerations of space should limit our statements to the merest indication of the process and the briefest record of the chemical result. The prodigious disproportion between

the meagerness of this fragment and the mass of detail which lies behind it in each case should be constantly before the mind of the reader. The book gives empirical knowledge, the laboratory work and the discussion of it furnish the only real knowledge. The extent and nature of this real knowledge may be shown in connection with any action. As an illustration we may point out some of the problems which the heating of potassium chlorate presents to one who is trying to acquire an intelligent acquaintanceship with its chemistry, and has not previously done the experiment.

First, the substance melts. It must be realized that this is a common occurrence which does not necessarily imply any profound change, and may be reversed by cooling. Later, the liquid appears to boil, and the properties of a boiling substance must be known. If the observer has been informed in advance that the body is homogeneous, he must know that, if it is simply boiling, it will evaporate completely and leave nothing behind, and that the temperature required to achieve this will remain constant from the beginning to the end. In order, therefore, to become aware of the fact that here decomposition is taking place, he must note the ways in which the decomposition of potassium chlorate differs from ordinary boiling. For example, if it were a case of boiling, he should expect to find the solid body condensing on the sides of the tubes, and note the fact that no such condensation is observed, with the appropriate inferences. He should observe that, in the later stages at least, the agitation of the liquid does not cease when the flame is removed, although this would undoubtedly occur in a case of simple boiling. He must further observe the changes in the consistency of the material and the way in which it finally becomes thick and may even solidify. Even the most experienced investigator would have to make many careful experiments before he could definitely classify the nature of the phenomenon being observed. The first inference would probably be that the phenomenon was certainly not one of mere ebullition. In some ways it is like the evaporation of a solution, obtained, say, by the melting of a substance in its own water of crystallization. Yet, this hypothesis would not explain to the thoughtful observer even the more obvious features of the phenomenon, for the liquid which was acting as a solvent would have to be amazingly volatile if the absence of any condensation on the walls of the tube was to be accounted for.

The illustration need not be elaborated further. These remarks are sufficient to show that even the simplest experiment presents an almost limitless field for the discussion of important questions which are more or less common to all chemical phenomena. It must be noted, also, that chemical change is in itself not perceptible by the senses, and that only physical properties and physical phenomena are observed (*cf.* pp. 36-40). The chemical facts, such as the general nature of the change, the conditions under which, and the facility with which it occurs, are reached solely by inference. The above example shows the ready and thorough knowledge of physics which must be at the command of every individual effort to study even the simplest chemical phenomenon. It is only when the physics as well as the chemistry of the change have been mastered that the "real knowledge" to which reference was made above has been gained.

Physical Properties of Oxygen. — Oxygen, as a gas, resembles air in being colorless, tasteless, and odorless. It is slightly heavier

than air; its density, using the physical standard of air = 1, is 1.105. The chemist often uses hydrogen as his standard, and oxygen is 15.900 times (Morley) as heavy. One liter of oxygen, at 0° and 760 mm. barometric pressure, weighs 1.42900 grams (Morley). The gas dissolves to some extent in water, the solubility at 0° being four volumes of gas in one hundred volumes of water (at 20°, 3 : 100). The critical temperature (*q.v.*) of oxygen is −118° C. At that temperature, fifty atmospheres pressure is required to liquefy it. Liquid oxygen, which was first made by Wroblewski, has a pale-blue color, and boils under one atmosphere at −182.5°. Its specific gravity at −182.5° is 1.13 (water = 1): that is to say, 1 c.c. weighs 1.13 g. By cooling with a jet of liquid hydrogen, Dewar froze the liquid to a snow-like, pale-bluish solid. The magnetic properties of the element are clearly shown by the force with which a tube of liquid oxygen is attracted by a magnet.

Specific Chemical Properties. — Under this head we describe the chemical behavior of a substance, enumerating the other substances, simple or compound, with which it unites or interacts (p. 14), stating the conditions peculiar to each action, and estimating the intensity of the tendency to chemical change in each case. In the case of a simple substance like oxygen we note particularly with how many of the other elements it can form compounds, how far it unites with them directly, and in how many cases the compounds have to be made by indirect means. In general, we call those simple substances **active** which unite with many other simple substances and do so by direct union. Oxygen, for example, is active, and nitrogen (*q.v.*) is relatively inert. The intensity of a chemical action is judged by its speed, by the electricity it can generate, or, roughly, by the heat evolved during its progress (p. 28).

Chemical Properties of Oxygen. — Sulphur, when raised in advance to the temperature necessary to start the action, unites vigorously with oxygen (Fig. 22), giving out much heat and producing a familiar gas having a pungent odor (sulphur dioxide). This odor is frequently spoken of as the "smell of sulphur," but in reality sulphur itself has no odor, and neither has oxygen. The odor is peculiar to the compound of the two. It may be added that the mode of experimentation can be changed and the oxygen led into sulphur vapor through a tube. The former then appears to burn with a bright flame, giving the same product as before.

Warm phosphorus combines with oxygen with even greater vigor, and forms a white, powdery, solid compound (phosphoric anhydride), which absorbs moisture from the aqueous vapor in the air and quickly forms a solution in this water. In both these cases the products differ from oxygen, not only in odor and in being a gas and a solid, respectively, but notably in that, when shaken with water, they dissolve and interact to form acids (see below).

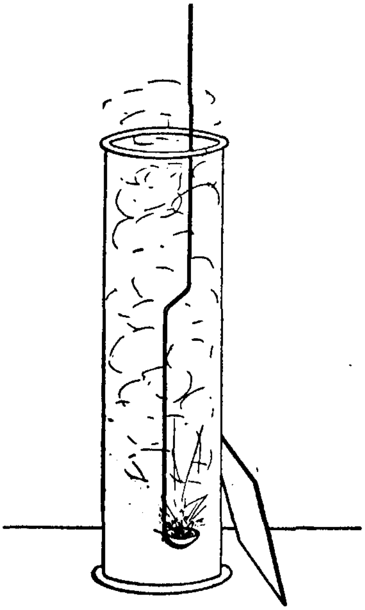


FIG. 22.

Burning carbon, in the form of charcoal, when plunged into the gas, glows much more brightly than in ordinary air. In this case the product is a gas (carbon dioxide). When this gas is shaken with "lime-water," a solution of calcium hydroxide $Ca(OH)_2$ (*q.v.*), a white precipitate of calcium carbonate $CaCO_3$ is formed.

Finally, metallic iron, which is simply rusted by air (diluted oxygen), burns in pure oxygen with surprising brilliancy. Globules of a molten product fall from the iron, and when they have cooled are found to consist of a dark-gray brittle material, which we recognize as identical with blacksmith's hammer-scale, and with a well-known ore of iron (magnetic oxide of iron).

Experiments like the above with the whole series of simple substances would show that oxygen unites in a similar way with nearly every member of the list, and often, though not always, with the same vigor as in the case of these examples. In the case of one or two elements, such as gold and platinum, the compounds are obtainable by double decomposition, and not directly. With the five members of the helium group, of which no chemical compounds are known, and with fluorine, oxygen does not combine. These three sentences summarize the chemical properties of oxygen.

Oxygen can unite with many of the same elements when they are

already in combination. Wood, for example, is composed of carbon and hydrogen, with a certain amount of oxygen. When previously heated, it is decomposed, and the constituents unite with oxygen forming carbon dioxide and water.

The Making of Equations Again. — To learn the exact nature of interactions like those used as illustrations above, quantitative experiments must of course be made and the usual method employed to obtain the formulæ of the products. Thus, for example, a known weight of sulphur is placed in a porcelain boat (Fig. 23), which has already been weighed. The U-shaped tube to the right contains a solution of potassium hydroxide which is capable of absorbing the resulting gas. The oxygen enters from the left. When the sulphur is heated, it burns in the oxygen, and the loss in weight which the boat undergoes shows the amount of sulphur consumed. The gain in weight of the U-tube shows the weight of the compound produced. By subtracting from this weight that of the sulphur, we get the quantity of oxygen. The proportion of the constituents and the steps in the calculation are as follows:

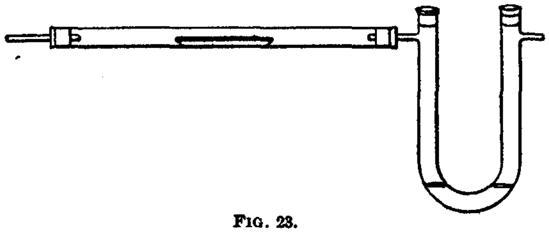


FIG. 23.

	PERCENTAGE*		AT. WT.		FACTOR			÷ 1.561
Sulphur,	50.05	=	32.06	×	1.561	=	S × 1.561	S × 1
Oxygen,	49.95	=	16.00	×	3.122	=	O × 3.122	O × 2

The formula of the product is therefore SO_2 and the equation $S + 2O \rightarrow SO_2$.

Similarly, phosphoric anhydride may be shown to have the formula P_2O_5, carbon dioxide CO_2, and magnetic oxide of iron Fe_3O_4.

The results given by the above experiment are usually inexact. The tendency to the formation of sulphur trioxide, often heightened by catalytic action (see

* Here the percentages are employed. The actual weights found in one experiment, however, may be divided by the atomic weights and the same result obtained (p. 65). In fact, any two numbers bearing the proper ratio to one another may be used.

below) of the porcelain of the boat, raises abnormally the proportion of oxygen. The principle of the experiment is easy to understand, however.

In the case of phosphorus a similar plan of experiment may be used. Instead of attempting to receive the solid product in a U-tube, however, it must be caught by a plug of glass wool in the main tube of hard glass, and a drying tube will be needed at the end to prevent admission of moisture from the air. The increase in weight of the hard glass tube represents the oxygen taken up. Care and leisurely performance are needed to make the experiment successful.

The measurement of the composition of carbon dioxide * gives the most exact results when carefully conducted. The data and working in these cases and in that of iron are as follows :

	Percentage		At. Wt.		Factor	÷ .704
Phosphorus,	43.66	=	31.0	×	1.408	P × 2
Oxygen,	56.34	=	16.0	×	3.521	O × 5
						÷ 2.272
Carbon,	27.27	=	12.0	×	2.272	C × 1
Oxygen,	72.72	=	16.0	×	4.545	O × 2
						÷ 0.431
Iron,	72.38	=	55.9	×	1.295	Fe × 3
Oxygen,	27.62	=	16.0	×	1.726	O × 4

The density of the vapor of phosphoric anhydride leads to the formula P_4O_{10}, but, as the substance is never used as a gas, the simpler formula is generally preferred.

Oxides. — Substances containing one element in combination with oxygen are called **oxides**, and processes like those described above are called oxidizing processes, or **oxidations**. When the same element forms more than one oxide, the names of the oxides indicate the differing proportions. Thus we have barium oxide (or monoxide) BaO, and barium peroxide (or dioxide) BaO_2, magnetic oxide of iron Fe_3O_4, ferrous oxide FeO, and ferric oxide Fe_2O_3. In cases like the two last the terminations *-ous* and *-ic* applied to the *metal* correspond to the smaller and larger proportions of *oxygen*, respectively, which the metal is able to hold in combination. Oxides of the form Fe_2O_3 are often called sesquioxides because they contain *one and a half* (Lat. *sesqui-*, one-half more) unit weights of oxygen to each one of iron.

Many oxides, like those of iron, are quite indifferent to water, but others, like those of sulphur and phosphorus, interact with it (see under Water). Some give sour solutions, containing acids dissolved in the excess of water. Such solutions turn blue litmus, a vegetable dye, red. Others give solutions with a taste like soap or borax, and here

* Described in the author's *Laboratory Outline of General Chemistry.*

the dissolved substance is called a base (*q.v.*), and turns litmus blue. Thus sulphur dioxide and phosphoric anhydride give sulphurous acid and phosphoric acid respectively:

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4.*$$

If the product, to whichever class it belongs, is not volatile, it may be obtained by evaporating the excess of water. In the case of sulphurous acid the above action is reversed by evaporation and the sulphur dioxide and water both pass off; in that of phosphoric acid, the white crystalline acid is obtained. In consequence of their relation to the acid, differing from it in *not* containing the elements of water, these oxides are often called **anhydrides**.

The discussion of the formation and properties of ozone (*q.v.*), which is an oxide of oxygen, cannot be taken up until we are in possession of the means of understanding the difference between the two substances.

Combustion. — Since oxygen is a component of the atmosphere, chemical actions in which it plays a part are familiar in daily life. Violent union with oxygen is called in popular language **combustion** or burning. Yet since oxygen is only one of many gaseous substances known to the chemist, and similar vigorous interactions with these gases are common, the term has no scientific significance. The union of iron and sulphur, even, gives out light and heat, and is quite similar in the chemical point of view to combustion.

In connection with this, however, it may be worth while to notice the distinction between combustible and incombustible substances. Things which are incombustible, using the term in its popular sense, may be divided into two classes. There are those substances which already contain all the oxygen which they can hold in combination. Such are the oxides whose formation we observed in the experiments described above. In everyday life, limestone, sand, bricks, and most rocks are illustrations. The other substances ordinarily classed as incombustible are those which do not unite with oxygen, as it is found in the air, with sufficient vigor. The iron used in the construction of fireproof buildings is the commonest example of this class.

* Here summation of the formulæ on the left would give $H_6P_2O_8$, but in such cases, unless there are reasons to the contrary, the common factor is put in front and the formula reduced to its lowest terms.

Oxidation. — The rusting of metals differs from combustion only in speed. Thus, magnesium ribbon, when left lying in the air, gradually becomes covered with a white crust. By scraping this off, and continually exposing the surface of the metal, the whole of the latter may eventually be transformed into the white powder. The product is identical in composition and properties with the oxide formed by combustion (p. 44). In the case of iron, burning gives us the magnetic oxide (Fe_3O_4), while rusting in moist air yields a hydrated ferric oxide ($Fe_2O_3 + Aq$*). The products differ in composition, but are closely related.

This process of slow oxidation, although less conspicuous than combustion, is really of greater interest. Thus the decay of wood is simply a process of oxidation whereby the same products are formed as by the more rapid ordinary combustion. Large volumes of pure water are mixed with sewage, the object being not simply to dilute the latter but to introduce water containing oxygen in solution. This has an oxidizing power like that of oxygen gas, and, through the agency of bacteria, quickly renders dissolved organic matters innocuous by converting them for the most part into carbon dioxide and water. In our own bodies we have likewise a familiar illustration of slow oxidation. Avoiding details, it is sufficient to say that the oxygen from the air taken into the lungs is carried by the blood throughout our tissues and is there used for oxidizing waste materials. The carbon dioxide is carried back to the lungs by the blood, and finally reaches the air during exhalation. To supply the place of the material thus removed, we are under the continual necessity of building new tissue from the food which we eat. If we cease to eat, we become lighter and weaker, showing that a real portion of our structure is gradually being consumed by oxidation.

The opposite of oxidation, the *removal* of oxygen, is spoken of in chemistry as **reduction**.

Means of Altering the Speed of a Given Chemical Action: By Change of Temperature. — That the same change may proceed with very different speeds according to conditions is a familiar fact. For example, **raising the temperature increases the rapidity of all chemical interactions**. Thus, cold iron combines with oxygen very slowly, giv-

* The formula H_2O may not be used excepting to indicate a definite proportion of the elements of water (18 parts). Where the proportion varies according to circumstances, as here and in the case of solutions, the contraction Aq is employed.

ing rust, while white-hot iron sheds quantities of scales of an oxide, formed in the few moments that it is under the blacksmith's hammer. White-hot coal unites with oxygen in the air to form carbon dioxide and seems to disappear before our eyes, while in the cellar, even in warm weather, we observe no appreciable diminution in its amount. The chemist, however, has reason for considering that even here the difference is one of degree only. No temperature can be found at which the interaction definitely begins. We believe that every change, provided, like these, it involves a liberation of energy (*cf.* p. 27), proceeds with *some* speed at every temperature. A rough estimation, based on experiment, shows that on an average, other things being equal, every rise in temperature of ten degrees doubles the amount of material changed per second, and conversely.

If, on bringing two materials together, the chemist observes no marks of chemical action, he immediately begins cautiously to *heat* the mixture. This appeal to the accelerating effect of a rise in temperature is always made as a matter of course.

The common expressions used in chemistry in describing temperatures, along with the corresponding readings of the thermometer, are as follows:

Incipient red heat,	about 525°.	Yellow heat,	about 1100°.
Dark red heat,	" 700°.	Beginning white heat,	" 1300°.
Bright red heat,	" 950°.	White heat,	" 1500°.

Rapid Self-sustaining Chemical Action and Means of Initiating it. — When a piece of wood is set on fire at one end, the heat produced by the action itself raises the temperature of neighboring portions until their speed of union becomes equal to that of the part originally lighted. In this way the whole becomes finally inflamed. When we blow the blaze out, the great excess of cold air suddenly lowers the temperature of the wood, and of the gas rising from it, and rapid union ceases. Whether a given set of materials can maintain itself at a temperature proper to violent interaction will depend on the amount of heat developed by the action itself on the one hand, and the losses of heat by conduction and radiation on the other. If the latter are great, the former must be greater. Thus the union of iron and oxygen *per se* gives heat enough to warm the materials to the burning temperature and leaves much over for radiation. But iron in air, which is four-fifths nitrogen, can receive the oxygen only one-fifth as fast at the start, and even more slowly as, later, the nitrogen accumulates round it. And be-

sides, all the nitrogen has to be heated to, perhaps, 2000°. The task is too great. The union is impeded and the iron is not oxidized fast enough to generate the heat required to maintain everything at this high temperature. Poor conductors of heat, like wood and candles, fare better. Powdered iron, with its particles presenting large surface to the air relatively to the weight of material in each particle to be heated, burns well.

The initial supply of heat required to *start* violent *exothermal* chemical actions, of which alone we are here speaking, must not be confused with the heat subsequently developed as the action proceeds. The latter is usually much greater. Indeed, the *preliminary supply* varies with circumstances, and may be made as small as we choose by limiting the area first heated and using ordinary precautions against radiation and convection. Indeed, in practice, a single spark from an induction coil often takes the place of more clumsy methods of raising the temperature. The heat *produced by the interaction itself*, however, is fixed in amount, and depends only on the materials and their quantity. Endothermal actions differ completely from those under discussion. In them a definite, large quantity of heat has to be furnished, and the action instantly ceases if the supply fails.

Heating is not the only means used to give the initial acceleration to a self-sustaining chemical change. The materials in a match-head are capable of undergoing a great transformation. Yet, so slowly does this proceed at ordinary temperatures, that matches may be kept in efficient condition for years. Here a rather violent vibration is employed to hasten the torpid action in a small part of the material, and the heat produced by the resulting action quickly ignites the whole. The same explanation accounts for the explosion of gun-cotton by a percussion fuse.

Other Means of Altering the Speed of a Given Chemical Change: By Change in Concentration; by Catalysis; by Solution. — Even when the temperature remains constant, there are other changes in the conditions (p. 52) which may be used for accelerating or for moderating the speed of chemical interactions. The most important of these is, a change in the **concentration** of the interacting substances. Another is the presence of a **catalytic** agent. The condition of **solution** might be accounted still another.

The abatement in the activity of the oxygen found in the air by the nitrogen which is mixed with it, is a question of **concentration** If the

concentration of pure oxygen under atmospheric pressure is taken as unity, that of oxygen in air is only about 0.2. And the speed of interaction of a body, other things being equal, is directly proportional to its concentration. This is not an obscure law, but merely common sense put into definite language. The *opportunity* which one substance has for getting at every part of another will be one factor in determining the speed with which the resulting transformation will take place. And this opportunity, other things being equal, depends on the thickness or density with which the substance is scattered in the region of action. In the case of a gas, this factor is measured by its partial pressure. Hence, lights burn badly at great elevations, where the oxygen is very tenuous. On the other hand, powdered charcoal interacts so rapidly when ignited in liquid air, where the oxygen is highly condensed, that an explosion takes place, whereas in common air it burns feebly. Again, when oxygen is compressed in contact with barium oxide at 700° it combines to form the dioxide (p. 64) ; when the pressure of the oxygen in contact with the latter is reduced, oxygen is liberated (see Chemical equilibrium).

When an extra substance increases the speed of a chemical change, seemingly by its mere presence, without itself suffering any permanent change, we call this **catalytic** (Gk. κατά, down; λύσις, the act of loosing) or **contact action**. The word was originally used for cases of decomposition. The foreign body is called the catalytic or contact agent, and the process catalysis. The effect of manganese dioxide on the decomposition of potassium chlorate (p. 65) is of this nature. When some of the chlorate is melted carefully, so as to avoid superheating, scarcely any evolution of oxygen can be perceived at this temperature (351°). If now a thin glass bulb filled with powdered manganese dioxide be broken in the molten mass, the oxygen is given off in torrents in consequence of the enormous acceleration of the decomposition. Yet the manganese dioxide itself may be recovered unchanged from the residue.

It is found that many actions owe what appears to be their normal speed to the presence of a trace of water vapor. Thus many of the elements show no visible tendency to unite with carefully dried oxygen, even when they are strongly heated in it. Addition of a trace of moisture, however, brings about instant combustion. So water is to be regarded as one of the commonest contact agents (see Chemical properties of chlorine).

A few cases of retardation of an action by a catalytic agent are known. Thus, a little benzyl alcohol or mannite added to the solution will retard the oxidation of

sulphites by the air. Hence positive and negative catalysis both occur (see abstract of an address by Ostwald in *Nature*, LXV, 522, given also in full in the *Zeitschrift für Elektrochemie* VII, 905).

The effect of **solution** in hastening a chemical change was seen when we examined the interaction of sodium chloride and silver nitrate (p. 13). With the solutions the action was seemingly instantaneous. If we had attempted to bring it about by rubbing the dry substances in a mortar, hours of work would have left much of the original bodies still unchanged. Even heating would not have produced so prompt an effect. It is obvious that the intimate access which every part of each solution gains to every part of the other accounts to some extent for the difference (see Ionization). Chemical actions, as will be seen in the sequel, are very frequently carried out in aqueous solution in order to take advantage of the favorable influence of this condition.

Thermochemistry. — As we have seen (p. 27), the free or available chemical energy of a system undergoing chemical change usually appears in the form of heat. Since it is often instructive to consider the amount of heat produced, some of the elementary facts of thermochemistry must be explained.

The chemical interactions to be studied thermally are arranged so that they may be carried out in some small vessel which can be placed inside another containing water. The heat developed raises the temperature of this water. Where gases like oxygen are concerned, a closed bulb of platinum forms the inner vessel. The quantity of heat capable of raising one gram of water one degree in temperature, between 0° and 100° Centigrade, is called a **calorie**. So that 250 grams of water raised 1° would represent 250 calories, and 20 grams of water raised 5° would represent 100 calories.

While in physics the unit of quantity is the gram, in chemistry the unit which we select is naturally that represented by the formula of the substance. Thus, the heat of combustion of carbon means the heat produced by combining twelve grams of carbon with thirty-two grams of oxygen, and is sufficient to raise 100,000 grams of water one degree. This is expressed as follows:

$$C + 2O \rightarrow CO_2 + 100,000 \text{ cal.}$$

In other words, the combustion of less than half an ounce of carbon will raise one kilogram (over two pounds) of water from 0° to the boiling-point.

It is always found that the same quantities of any given chemical substances sustaining the same chemical change under the same conditions produce or absorb, according as the action is exothermal or endothermal (p. 27), amounts of heat which are equal.

The *rate* at which a given chemical action is allowed to take place has no influence on the total amount of heat consumed or produced. It may not at first sight appear obvious that rusting evolves heat, but a delicate thermometer would show that a heap of rusting nails was somewhat higher in temperature than surrounding bodies. Poor conductors, like oily rags and ill-dried hay, show a tendency to spontaneous combustion owing to accumulation of the slowly developing heat of oxidation. The warmth of our own bodies is in part due to the same cause.

In accordance with invariable experience expressed in the law of the conservation of energy, when an action is chemically capable of reversal, the contribution of the same amount of heat which it develops will exactly suffice to drive the chemical change in the opposite direction. The heat contributed is simply used to restore the amount of chemical energy proper to the original system. Thus, the union of one chemical unit weight each of mercury and oxygen (p. 62) produces 30,600 cal.:

$$Hg + O \rightarrow HgO + 30{,}600 \text{ cal.},$$

and the decomposition of one formula-weight of mercuric oxide (p. 12) demands the same amount of heat in order that free mercury and oxygen, with their appropriate proportions of chemical energy, may be recovered.

In practice it is found that all chemical changes are not capable of reversal by the use of the sources of heat available in the laboratory. A quantity of heat, equivalent to that produced by any chemical action on a small scale, is very easily provided, but something more appears to be necessary. The heat provided must be of a certain *temperature*, otherwise it is quite ineffective. For example, the heat produced by the union of calcium and oxygen is within the limits of ready measurement,

$$Ca + O \rightarrow CaO + 131{,}000 \text{ cal.},$$

and the supply of this amount (or even of unlimited amounts) of heat to calcium oxide (quicklime) is easily achieved. Yet this method is quite ineffective to produce decomposition (p. 63) of the product.

Apparently we have not sufficiently high temperatures for the purpose at our command (see Factors of energy).

It may be noted in this connection that the temperatures required to produce reasonably rapid decomposition vary within a wide range. Some substances can be kept only below 0°, and decompose when allowed to become warm. Others, like the oxides of gold and platinum, require a little heating (p. 63). Many, like quicklime, are not broken up even at the temperature of the electric arc. When the energy is applied in the form of electricity (p. 19), instead of heat, the range is incomparably more easily within the reach of the means ordinarily at our disposal. There is no substance, provided it is of such a nature as to be affected by the electric current at all, which cannot be decomposed by a current with an E.M.F. of 10 volts or less, while currents of 110 volts and over are commonly accessible. It is partly on this account that electrical processes have become so common in industrial chemistry.

One of the most important principles of thermochemistry is the **law of constant heat summation.** If a system of substances can be transformed into another system of substances by different stages or by more than one route, then the algebraic sum of the heats absorbed or produced in the various stages is the same. Thus, barium oxide might be formed directly from the proper proportions of the constituents, or it might be made by preparing the dioxide (p. 63), and then driving out half of the oxygen contained in the latter. The quantities of heat involved in these changes are as follows:

$$Ba + O \rightarrow BaO + 124{,}400 \text{ cal.} \qquad (1)$$

$$\begin{cases} Ba + 2O \rightarrow BaO_2 + 141{,}600 \text{ cal.} & (2) \\ BaO_2 \rightarrow BaO + O - 17{,}200 \text{ cal.}^{*} & (3) \end{cases}$$

When the last two equations are added algebraically, canceling terms such as BaO_2 and O, which are common to both sides of the final equation, the chemical action is seen to be the same as in (1), and the balance, in favor of heat produced, is 124,400 calories as before. If in such cases the sum of the heats was not the same, it would follow that by using different plans of procedure we could prepare different specimens of the same substances containing different proportions of chemical energy. This, however, we have never been able to do (p. 77).

* Since (3) is to be added to (2) so as to give (1), the formulæ of (3) must be so placed that if the initial substances of (1) are on the left side of (2), the products of (1) may be on the right side of (3) and *vice versa*.

The quantities of heat liberated in two chemical changes are often measures of the relative amounts of available chemical energy in the systems before the change, and, therefore, often furnish a measure of the relative chemical activities of the two sets of substances. The comparison may safely be made in certain cases when the conditions under which the two actions take place are precisely alike. Formerly it was supposed that the heat liberated was always proportional to the chemical activity of the substances, but we have already shown cause (pp. 27–28) why this general statement cannot be true.

Exercises. — 1. Construct the equations for the combustion of phosphorus, carbon, and iron in oxygen (p. 70).

2. When 1 g. of sodium burns in oxygen, it produces 1.7 g. of the oxide. What is the formula of the latter, and the equation (p. 69)?

3. Which are the components (p. 34) of the liquid made by treating phosphoric anhydride with water? Which are the constituents (p. 34) of phosphoric acid?

4. How should you show that, in the making of oxygen from a mixture of potassium chlorate and manganese dioxide, the latter remains unchanged? Which properties (p. 37) are you employing for this purpose?

5. Discuss the union of iron and sulphur (p. 11) and the decomposition of mercuric oxide (p. 12) in their relation to the explanations on pp. 73–74.

6. How many calories are required to raise 500 g. of a substance of specific heat 0.5 from 15° to 37° (p. 76)?

7. The combustion of 1 g. of sulphur to sulphur dioxide develops 2220 calories. What is the heat of combustion of sulphur (p. 76)?

8. Outline briefly the proof that thermochemical data are not accurate measures of chemical activity (p. 79).

CHAPTER VI

THE MEASUREMENT OF QUANTITY IN GASES

We have spoken of measuring the proportion by weight of the oxygen used in several chemical changes, but in our illustrations we have never weighed the gas itself. We have always (*e.g.* p. 69) obtained its quantity by subtracting the weights of solid or liquid bodies. In practice this method often serves the purpose.

Our preference for weighing as a means of ascertaining quantity of matter is largely due to the fact that the weight is independent of the physical or even chemical condition of the substance. Yet, with proper precautions, we may learn the quantity of matter by means of any other attributes which are proportional to it. Now the volume is such an attribute. In determining the quantity of a liquid, where rapidity with no great accuracy is desired, the volume is frequently measured. In the case of gases the error made in measuring the volume is less, as a rule, than in measuring the weight.

The Variable Concentration of Gases. — A little experience with gases soon shows us that measurement of volume alone does not necessarily give any definite idea of the quantity of matter present. The denseness with which the gaseous matter is packed (the **concentration** of the gas) in the vessel must somehow be defined, as well as its volume, in order that there may be specification of the quantity of matter.

Gases vary markedly in chemical activity with changes in their concentration (*cf.* p. 75), and thus the consideration of this condition (p. 52) is continually forced upon the chemist. Solids and liquids do not alter their denseness of packing (concentration) very noticeably even when compressed severely or changed in temperature. So that concentration need not be considered in the case of pure bodies in the solid or liquid forms. Such substances can be scattered through a variable space by solution in some suitable solvent, however, and then their degree of packing or concentration becomes an important factor in *their* chemical behavior also.

The principle used for estimating the concentration of a gas may be illustrated by means of the arrangement in Fig. 24. Except that

a little gas (any gas will do) remains shut off by the mercury in the left limb of the tube, the whole apparatus has been evacuated. The reservoir can be turned upward, and thus larger amounts of mercury may be introduced into the tube.

Now the portion of the mercury below the dotted line is essentially a balance, that is to say, it will move in one direction or the other if the stresses on either side change. At present these stresses must be equal. On the right pan of the balance, so to speak, the stress is represented by the weight of the column of mercury above the dotted line. As there is nothing in the tube above this mercury, the weight of the latter is all that this side of the balance sustains. On the left pan of the balance there must be an equal stress, and this stress can be caused only by the gas confined in the shorter limb. The nature of a gas suggests that this stress must be exercised on the walls of the tube also, although they naturally do not exhibit its effects. This stress we call the **pressure** or **tension** of the gas.

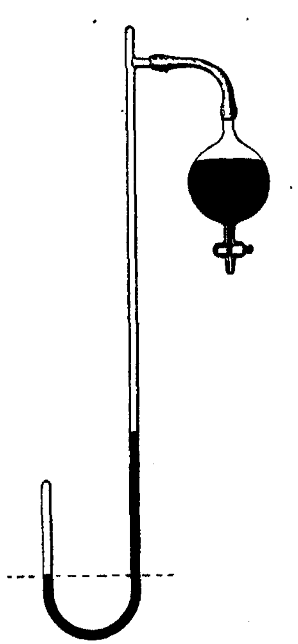


FIG. 24.

The height of the surface of the mercury on the right above that on the left having been measured, more mercury may now be added from the reservoir, and the difference in the two levels again noted. The gas cannot have diminished in amount, yet it now occupies a smaller space, and is, therefore, packed more closely — its concentration is greater than before. If, for example, the difference in level is now twice as great, it will be found that the concentration of the gas is also twice as great (its volume having become half of the original volume). Whatever amount of mercury is added, we shall always find that the concentration of the gas is proportional to the height of the mercury. But this in turn is proportional to the weight of metal. The weight of mercury on one side must, therefore, be equal to the stress or pressure or tension of the gas on the other side which balances it. Hence, **the concentrations of a sample of any gas are proportional to the corresponding pressures it exercises.** We

determine, therefore, the denseness with which any sample of gas is packed by measuring its pressure.

Method of Allowing for Varying Concentration in Measuring Quantity in Gases. — The principle just stated is applied to the measurement of the quantity of matter in a sample of gas by permitting the concentration of the sample to alter until it is equal to that of the atmosphere at the moment. Then we read off the volume now occupied, and simultaneously we ascertain the pressure by observing that of the atmosphere. Each of these two operations is facilitated by a special arrangement of apparatus.

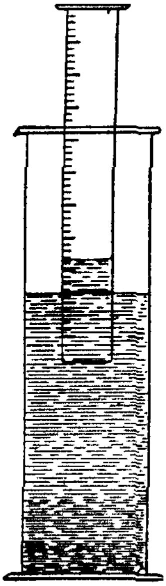


FIG. 25.

A gas to be measured is always confined so that some liquid constitutes one part of the barrier to its escape. The very simplest form of the apparatus is shown in Fig. 25. To render the concentration (and pressure) of the gas equal to that of the atmosphere, the cylinder containing the gas is lowered (or raised) until the levels of the liquid inside and outside are the same. When the system is in this condition the stress of the gas on the inner surface must be equal to that of the atmosphere on the outer one, otherwise movement of the liquid would occur. The volume of the gas is then read directly from the graduation on the cylinder. Often the cylinder, or other vessel, is closed with a ground-glass plate, placed quickly in erect position, and weighed. The weight of water which is then required to fill it to the brim gives more exactly the volume occupied by the gas (1 g. water = 1 c.c.). When special modes of admitting or handling the gas have to be provided for, the apparatus may be more complex. But the principle of adjustment is always the same. In exact work, mercury is employed *to confine the gas. Water serves the purpose of rough work with* gases which, like oxygen, are but slightly soluble in it. When water is used, the volume is too great by the space occupied by the vapor of the water which is mixed with the gas (see Mixed gases), and a correction must always be made on this account.

The pressure or tension of the atmosphere at any moment is meas-

ured by means of a simplified form of the apparatus in Fig. 24. The reservoir is omitted. The atmospheric air being the gas whose concentration is to be measured through its pressure, the short limb is left open. The resulting apparatus (Fig. 26) performs its functions in the same way as does the more complex one. The only difference is that mercury is *automatically* added to or withdrawn from the right side by the motion of the metal resulting from changes in the pressure of the air. The reading of the vertical height between the lower and upper surfaces of the mercury gives a number which is proportional to the weight of mercury on the right side of the balance and, therefore, to the (equal) stress of the atmosphere on the left. This is called the *barometric reading* (uncorrected), after the name of the instrument.

To make different readings, taken when the mercury is at different temperatures, strictly proportional to the weight of the metal, the observed height is always *reduced* to that which would have been shown by the same weight of mercury at 0° in the same apparatus. A thermometer, and a table of temperatures with the corresponding corrections to be subtracted from the uncorrected reading (C, Fig. 26), must be used.

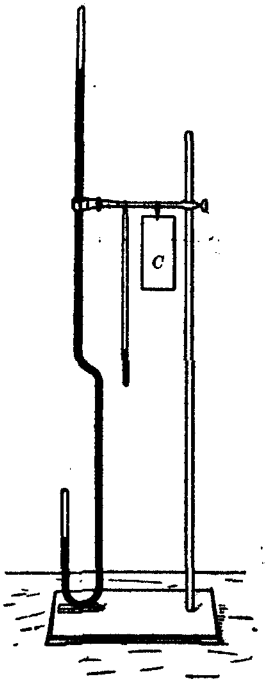


FIG. 26.

Knowing now the volume occupied by the sample of gas when its concentration is equal to that of the atmosphere and the barometric reading, which is proportional to this concentration, the measurement of the amount of matter in the sample has become definite so far as concerns the variability of concentration with change in pressure.

The recorded results of measurements made as above at different times are still unsatisfactory because the data for samples of the same kind of gas differ in the value of the pressure as well as in that of the volume. To make the results easily comparable in respect to the amount of matter they represent, one further step is needed. All the data are recalculated so as to show the volume each sample would

have occupied if the pressure had been equal to the weight of 760 mm. of mercury, which is the average height of the barometer at the sea level in 45° of latitude.

We have seen that the concentration of a given quantity of a gas is proportional to its pressure (p. 81). But, volume occupied is the inverse of concentration. Thus the same rule may be stated in the form, **the volumes occupied by a sample of any gas are inversely proportional to the pressure at each volume.** The fact was discovered by Boyle (1660) who stated it in this way. In still other words, the product of the several pressures and corresponding volumes of a sample of gas is a constant.

A numerical illustration will show the mode of applying this rule. We measure 200 c.c. of a gas at atmospheric pressure, and the barometer reads 742 mm. The question is: What would be the volume of this amount of gas at 760 mm. barometric pressure? It will be $200 \times \frac{742}{760}$ c.c. = volume at 760 mm. It is unnecessary to use any formula, but absolutely essential to ask: Is the new pressure greater or less than the old? Here it is *greater*. Hence, according to the law, the new volume will be *less*, so that the fraction must be arranged with the smaller number in the numerator.

Boyle's law may be illustrated by using a long tube bent like a barometer (Fig. 26) but having the short limb closed and the long one open. Strips of paper mark the levels of the mercury, which are at first alike on both sides, and register the volume of the air in the short limb at a pressure of one atmosphere. The reading of the barometer at the time, say 750 mm., is noted. Then mercury is added through a funnel inserted in the long limb, until the level in this limb is 750 mm. above that in the other. A stick cut to 750 mm. length, and held beside the tube, will conveniently show when this has been accomplished. The pressure in the open limb being now two atmospheres, the volume of the air will be found to have diminished to one-half its former value.

For pressures lower than one atmosphere, a different arrangement must be used. A graduated tube, closed at one end, is partly filled with mercury and inverted in a tall, narrow cylinder full of the same metal. The tube is then clamped in any position, such that the mercury level in the tube is above that in the cylinder. The reading of the barometer is next noted. The volume occupied by the air in the tube is then read, and the difference in height of the two mercury surfaces is measured by means of a graduated rule. Subtracting this height from that of the barometer gives the pressure of the air in the tube. The position of the tube is then altered, and the same measurements repeated, as often as is wished. The product of each volume and the corresponding pressure will be a constant number. The law is expressed mathematically by letting p_1 and v_1 represent the initial pressure and volume, p_2 and v_2 the new pressure and volume, and so forth. Then $p_1v_1 = p_2v_2 =$ constant for that particular specimen of gas. For a given sample of gas, any one of the four values may be calculated if the other three are known.

Boyle's law states the facts with sufficient accuracy for all ordinary purposes. But in reality no two gases behave *precisely* alike in respect to change in concentration when the pressure is altered (see Molar weights). The same gas does not even behave in precisely the same way at high, intermediate, and low pressures. The ideal gas, which should behave uniformly, we call the *perfect* gas. With most gases, at low pressures concentration increases more, and at very high pressures much less than the rule indicates (see Kinetic hypothesis).

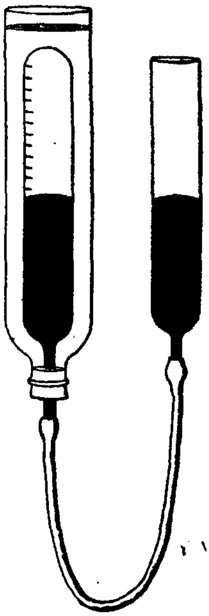


FIG. 27.

The Relation of the Volume of a Gas to Temperature. — In the foregoing we have assumed that there were no temperature effects. But, as a matter of fact, a rise in temperature will at once produce an increase, and a fall in temperature a decrease in the pressure of an inclosed sample of a gas. Hence a record of the pressure alone will fail to indicate the concentration definitely, and volume and pressure together will still leave the amount of material unspecified. The temperature must, therefore, be given as well.

Our descriptions of different samples of gas having thus become once more incomparable, we apply the same kind of remedy as before. We calculate the volume which each specimen of gas would occupy at 0°.

The rule for this calculation may be demonstrated in a rough way as follows: The large, graduated bulb (Fig. 27) is surrounded by a vessel which can subsequently be filled with ice water or with water of any temperature up to 100°. About one-half of its volume is occupied by the gas. The mercury which fills the rest is connected with a reservoir, so that the levels of the metal can be made alike, and the pressure of the gas be maintained constantly the same as that of the atmosphere. When, now, the volume occupied by the gas at 0° is read, and warmer water is introduced, we find that the volume gains $\frac{1}{273}$ of its value at 0° for every degree through which its temperature rises. If it is cooled below 0°, it loses $\frac{1}{273}$ of its volume at 0° for every degree through which the temperature is lowered. Observation gives practically the same value for all gases.

The following graphic method will put these facts in a clearer light. In Fig. 28 we have on the left a thermometer scale divided

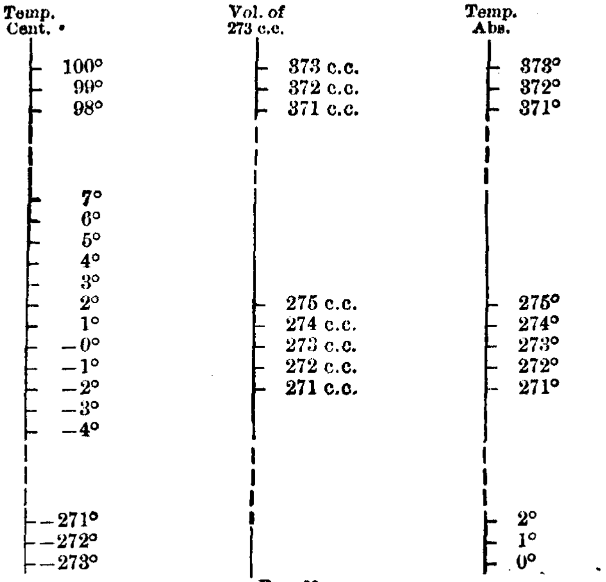


Fig. 28.

into degrees Centigrade. The middle line represents the volumes of a given sample of gas which correspond with the successive temperatures. If we, for convenience, take a volume of 273 c.c. of a gas at 0° and warm this through 1°, then at 1° its volume, having gained $\frac{1}{273}$ of its original value, becomes 274 c.c. At 2° it has gained another $\frac{1}{273}$ of the volume it had at 0° and becomes therefore 275 c.c., etc. If cooled below 0° it loses $\frac{1}{273}$ of the volume, becoming 272 c.c., etc.

If the gas be heated to 100° it gains $\frac{100}{273}$ of its volume at 0° and becomes 373 c.c. We might infer that if it were cooled through 273° from 0° it would lose $\frac{273}{273}$ of its volume, in other words, it would disappear. This temperature has not yet been reached, and in any case all gases would presumably liquefy before reaching it. Our statements apply to ordinary temperatures only, and within them the law holds with considerable strictness. Now the series of numbers on the middle line (Fig. 28) are all 273 units larger than the temperatures Centigrade in the line to the left of the figure. If we alter the graduation of the Centigrade thermometer by adding 273 to each temperature,

we secure the scale on the right, which exhibits degrees of the very same length as before, but has the additional advantage that the numbers expressing temperature are the same as those expressing volume. This is what we call the **absolute scale of temperature.** In this artificial case we started with 273 c.c. at 0° C. (273° Abs.), and the absolute temperature is here always numerically equal to the volume. If a different volume had been taken at 0°, then the volume assumed by the gas at each temperature would have borne a constant ratio to the volumes recorded. Hence, **the volumes assumed by a sample of gas at different temperatures, the pressure remaining constant, are in the same proportion as the corresponding absolute temperatures.** This is the modern way of stating a fact which was first discovered by Charles of Paris (1787). Obviously, if the *volume* remains constant, then the *pressure* will be proportional to the absolute temperature. The bare fact underlying our statement of the law is that **all gases suffer equal increments (or decrements) in volume (or pressure) for equal changes in temperature.**

The discovery of this fact is generally attributed to Dalton, who first published an investigation of the subject, embodying this result, in 1801, or to Gay-Lussac, who made a more complete investigation in 1802. Inasmuch, however, as in Chemistry we have another important principle known as Gay-Lussac's Law, and several which are connected with the name of Dalton, it is on the whole fortunate that we are justified in attributing this discovery to Charles.

The application of this law may best be illustrated by an example. We obtain 200 c.c. of a gas at 20° and wish to know what volume it would occupy at 0°. To answer the question, we convert the Centigrade temperatures to the absolute scale by adding, algebraically, 273 to each. Thus 200 × $\frac{273}{293}$ = the volume at 0° required. No formula is needed. We simply ask whether the new temperature is higher or lower than the old one. Here it is *lower*. The new volume will therefore be *smaller* than the old one. So we take care to place the smaller number in the numerator.

The law may be put in mathematical form thus: If we make v_0 the volume at 0° and v_1 the volume at the temperature t_1, then

$$v_1 = v_0 + \frac{1}{273} v_0 t_1 = v_0 \left(1 + \frac{1}{273} t_1\right) = v_0 \left(\frac{273 + t_1}{273}\right).$$

The number $273 + t_1$ is the value of the temperature increased by the number 273, and the sum is spoken of as the absolute temperature. The intervals between the degrees on this scale are the same as those on the Centigrade thermometer, but the numbers corresponding to them are all increased by 273. Using T_1 for the absolute temperature corresponding to $t_1°$, the last expression, above, becomes equal

to $v_0 \frac{1}{273} T_1$. Now, similarly, for any other temperature, T_2, there will correspond another volume, v_2, and the same relation will hold, namely, $v_2 = v_0 \frac{1}{273} T_2$. Equating both values of v_0 and calling $\frac{1}{273}$, the coefficient of expansion, a, we get,

$$\frac{v_1}{aT_1} = \frac{v_2}{aT_2} \text{ or } \frac{v_1}{v_2} = \frac{aT_1}{aT_2} \text{ or } \frac{v_1}{v_2} = \frac{T_1}{T_2}.$$

In words, *the volumes occupied by a sample of a gas are proportional to the absolute temperatures.* The last formula enables us to calculate any one of the four values when we know the other three. It is preferable, however, that beginners should use the method employed in the illustration given in the preceding paragraph. Simple mathematical expressions, like the one representing this law, are not made to save us the trouble of remembering the law itself, and it would be unfortunate if their use led us to forget it.

An instructive graphic demonstration of the law is given by Ostwald in his *Principles of Inorganic Chemistry*, p. 75.

The behavior of gases in respect to changes of temperature and pressure are perfectly independent of one another, so that the above laws may be applied to any example, either in succession, using the answer for the first calculation in making the second, or simultaneously. Thus 200 c.c. of gas at 742 mm. pressure and 20° become $200 \times \frac{742}{760} \times \frac{273}{293} = 183.8$ c.c. at 0° and 760 mm.

Mixed Gases. — Two gases at the same temperature, provided they do not interact chemically, do not interfere with each other's pressures when mixed. Thus, if they are forced into the same volume, the pressure of the mixture is equal to the sum of those of the components (Dalton's law, 1807). The gases are therefore still thought of individually, and the share which each gas has in the total pressure is called its **partial pressure**. This, like any other gaseous pressure, is proportional to the concentration of the particular gas in the mixture.

For example, a gas measured over water contains water vapor. The partial pressure of this, called the aqueous tension (*q.v.*), which is definite for each temperature, must be subtracted from the total pressure. The remainder is the partial pressure of the gas being measured, and this remainder is used as the pressure of this gas in any calculation.

Densities of Gases. — The application of the laws of Boyle and Charles enables us to express the quantities of matter in samples of gases in a definite and readily comparable manner. In describing chemical changes, however, it is continually necessary to express quantities of gases by weight. The relation between volume and weight for each kind of gas must, therefore, be ascertained. If we

know, for example, the weight of one liter of each gas at 0° and 760 mm. pressure, conversion to other weights, volumes, temperatures, and pressures can be made. The one-thousandth part of this value, the weight of 1 c.c., is called the **density** of the gas. Often, however, the relative weights of equal volumes, with that of air or hydrogen as unity, receive this name.

For most chemical purposes a high degree of accuracy is not required. Different arrangements of apparatus are used according to circumstances. The most direct method is to employ a light flask provided with a rubber stopper and stopcock (Fig. 29). By means of an air-pump the contents of the flask are removed, and it is weighed. This gives the weight of the empty vessel. The gas, whose density is to be ascertained, is then admitted, and care is taken that it finally fills the flask at the pressure of the atmosphere. The flask is closed and weighed again. The increase represents the weight of the gas. At the same time the temperature and barometric pressure are read. The volume is determined by displacing the gas once more from the flask, filling with water, and weighing again. The difference in weight between the empty flask and the flask full of water, in grams, represents the volume of the content of the flask in cubic centimeters. This volume is reduced to 0° and 760 mm. by the rules discussed above, and we have then a volume of the gas and the corresponding weight.

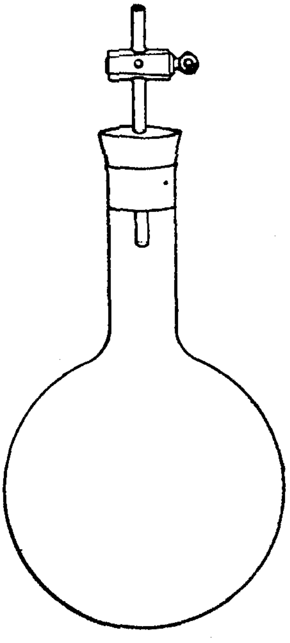


FIG. 29.

To illustrate, let us suppose that the volume of the flask is 200 c.c. and that it is filled with oxygen at 20° and 742 mm. The weight, we will suppose, is found to be 0.26 g. We ascertained (p. 88) by calculation that at 0° and 760 mm. this volume would be 183.8 c.c. The weight of a liter is given by the proportion $183.8 : 0.26 :: 1000 : x$. Here $x = 1.415$ g. When the operation is performed carefully, and the weighing carried to the nearest milligram instead of the nearest centigram, a result more nearly approaching the exact one (1.429) may easily be reached.

To get the density of oxygen referred to hydrogen as unity, we must divide the answer by the weight of a liter of hydrogen (0.08987 g.). In the above case the quotient is 15.74. The accepted value is 15.90. The density referred to air as unity is similarly obtained by dividing by 1.293, the weight of a liter of air at 0° and 760 mm. pressure.

If a suitable pump is not available, the flask, in this case provided with two openings, is weighed without preliminary exhaustion. This gives the weight of the vessel *plus that of the air it contains*. A continuous stream of the gas is then passed into the flask until the air has been completely displaced. The vessel is then closed and another weighing made. Finally the gas is displaced by water, and a third weighing taken. The temperature and barometric pressure are noted as usual. The last weighing gives the volume as before. Knowing that one liter of air weighs 1.293 g. at 0° and 760 mm., we may calculate readily the weight of the air which the flask contained at the observed temperature and pressure. When this is subtracted from the number obtained in the first weighing, we have the weight of the empty flask. Subtracting this in turn from the second weighing, we have the weight of the gas. We obtain thus the weight of a known volume of the gas at a known temperature and pressure, and finish the calculation as before.

The values of the densities of gases are of great significance in the chemical point of view. A number of them are given in connection with the discussion of molar weights (*q.v.*).

Vapor Densities of Liquids and Solids. — The densities of vapors are as important to the chemist as those of gases and, solids and liquids being more numerous, are even more frequently measured.

The apparatus must be specially adapted to the purpose. In its simplest form (Dumas' method) it consists of a bulb (160–200 c.c.) provided with a long, narrow tube (Fig. 30). This corresponds to the flask used for gases. The bulb is first weighed *full of air*, and is then charged with a considerable amount of the substance, usually a liquid. It is then suspended in a bath whose temperature can be maintained at some point above the boiling-point of the substance. Boiling water (100°) serves for liquids boiling below 100°. When the vapor has expelled all the air, and is no longer seen to issue from the tube, the bulb contains nothing but the vapor. The tip of the tube is then sealed with a blow-pipe. The temperature of the bath is taken and the barometer is read. When the bulb has cooled, it is weighed for the second time. The tip of the tube is next filed off under water, which rushes in and fills the bulb almost entirely. A third weighing, which should include the portion of the neck filed off, gives, after subtraction of the weight of the vessel, the content of the bulb. From

the content and the temperature and pressure at the time of the first weighing, we calculate the weight of air which the bulb originally contained. *When this is subtracted*, we obtain the weight of the empty bulb. Subtracting that in turn from the second weighing, we get the weight of the substance which, in the state of vapor, just filled the bulb at the temperature of the bath (say 100°) and at the pressure indicated by the barometer. From these data we calculate the density referred to hydrogen (or air) as unity.

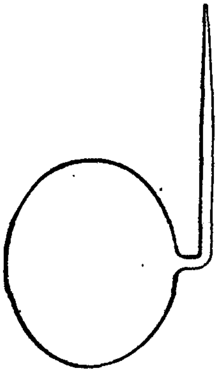


FIG. 30.

The reduction to 0° and 760 mm. pressure by rule gives, of course, a fictitious result. The vapor would condense to the liquid form before 0° was reached, if the cooling were actually carried out. But the value for the density *as it would be* at 0° and 760 mm. has to be calculated to facilitate comparison with the corresponding values for other substances. The results have no physical significance, but are highly important to the chemist.

Exercises. — The foregoing cannot be understood unless some problems involving the laws of gases are actually worked.

1. Reduce 189 c.c. of gas at 15° and 750 mm. to 0° and 760 mm.
2. Reduce 110 c.c. of gas at – 5° and 741 mm. to 0° and 760 mm.
3. Convert 500 c.c. of gas at 25° and 700 mm. to 18° and 745 mm.
4. A Dumas bulb full of air weighs 13.3125 g. After being filled with the vapor of carbon tetrachloride at 100°, it weighs 13.7969 g. Filled with water it weighs 141.3 g. The barometric reading (corr.) is 755 mm. What is the vapor density referred to air at 0° and 760 mm.?
5. The density of a substance referred to air is 3.2. What is the density referred to hydrogen? What will be the volume occupied by 10 g. of the substance at 20° and 752 mm.?

CHAPTER VII

HYDROGEN

HYDROGEN, although discovered by Paracelsus in the sixteenth century, was confused with other combustible gases, and its independent nature was first established by Cavendish in 1766. Somewhat later (1781), the latter showed that hydrogen when it burned gave water vapor, of which he condensed a large quantity to the liquid form. Taken in conjunction with Lavoisier's proof that oxygen was the active substance in the air (1777), this fact showed that water was a compound and not a simple substance. The new element was named hydrogen (Gk. ὕδωρ, water; γεννᾶν, to produce).

Occurrence. — The free element is found, mixed with varying proportions of other gases, in exhalations from volcanoes, in pockets found in certain layers of the rock-salt deposits, and in some meteorites. The air contains a mere trace of it, not more than one part in 30,000. Its lines are very prominent in the spectrum of the sun and of most stars.

In combination, it constitutes about 11 per cent of water. It is an essential constituent of all acids. It is contained also, in combination with carbon, in the components of natural gas, petroleum, and all animal and vegetable bodies.

We have seen (p. 83) that, using the physical unit of weight, which is the same for all substances, the element hydrogen stands ninth in order of plentifulness. But the *chemical* work that elements can do should rather be reckoned by the relative numbers of atomic weights which are available. When Clarke's numbers are recalculated to this basis, and the number of chemical unit weights of oxygen is called 100, hydrogen assumes a position more in harmony with its importance:

Oxygen	100.00	Aluminium	8.57	Iron	2.97
Hydrogen	30.10	Magnesium	3.29	Calcium	2.81
Silicon	28.52	Sodium	3.17	Potassium	2.64

Acids. — In making hydrogen, the acids are used almost exclusively. Hence, some statements in regard to their nature must be made before we can use them intelligently.

The common acids are hydrochloric acid (HCl, Aq), sulphuric acid (H_2SO_4, Aq), and nitric acid (HNO_3, Aq). The usual forms are mixtures containing water, the variable amount of the latter being indicated by the symbol Aq. The first is a solution of a gas, hydrogen chloride. The "pure concentrated" hydrochloric acid used in laboratories contains nearly as much of the gas (39 per cent by weight) as the water can dissolve. When heated, it readily gives up part of the gas, and the effervescence attending this must not be mistaken for evidence of chemical action. The "commercial" acid contains impurities and is also less concentrated. The "concentrated" sulphuric acid is an oily liquid containing practically no water. The "commercial" sulphuric acid contains 6 to 7 per cent of water, besides impurities. The "pure concentrated" nitric acid contains 70 per cent of liquid nitric acid. The "commercial" acid, 53 to 62 per cent and impurities in relatively small amounts. Acetic acid ($HC_2H_3O_2$, Aq) is a solution of a liquid in water. All the "dilute" acids contain 90 to 95 per cent of water. The water, as a rule, takes no part in the chemical changes in which the acids are concerned, and is therefore omitted from the equations.

The name "acid" is restricted to one class of substances having certain definite characteristics. Hydrogen is the only essential constituent of all acids. When free from water they do not conduct electricity. Their aqueous solutions have a sour taste and change the color of litmus from blue to red. We shall note presently two other properties which acids show when dissolved in water: — They conduct and are decomposed by the electric current, and their hydrogen (or one unit weight of it in the case of acetic acid) is displaced by certain metals.

In describing the chemical behavior of acids, we speak of the material combined with the hydrogen as the negative **radical** (see next section). Thus the negative radicals in the above acids are Cl, SO_4, NO_3, and $C_2H_3O_2$, respectively. The first (Cl) is a simple radical, the others complex. In many interactions the complex radicals move as units from one state of combination to another.

Preparation of Hydrogen by Electrolysis. — A supply of free, unmixed hydrogen not existing, we are compelled to prepare it from compounds by the two general plans (p. 63) used for liberating simple substances. When the first plan, the direct application of energy, is employed, we find that electricity serves the purpose best.

$$Sn + 2HCl \rightarrow 2H + SnCl_2$$
(Tin) (Stannous chloride)

$$Al + 3HCl \rightarrow 3H + AlCl_3$$

The water undergoes no change during the action, although its presence is essential. It is simply a part of the apparatus. Any acid may be used, although with many the action goes on very slowly. In all cases the plan of the action is the same: the metal is said to *displace* the hydrogen (see below).

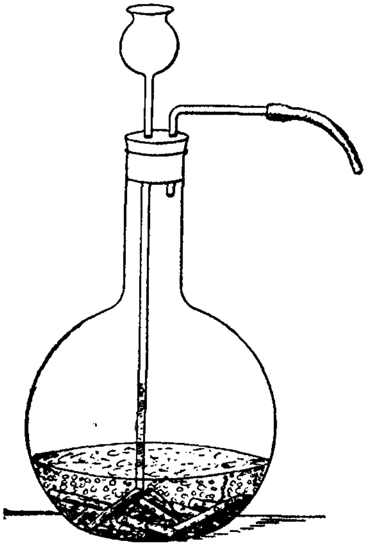


Fig. 32.

The apparatus for generating small amounts of hydrogen (Fig. 32) is arranged so that additional acid may be added through the thistle or safety tube. This avoids admission of air. With a Kipp's apparatus (Fig. 33) the gas may be made on a larger scale and its delivery can be regulated. When the stream of gas is shut off by the stopcock, the pressure of the gas, as it continues to be generated, drives the acid away from the metal and up into the globe above, so that the action ceases. Yet the action is ready to begin again the moment any portion of the stored gas is drawn off for use.

A rather sharp line can be drawn between those metals which displace hydrogen from dilute acids and those which, like mercury, silver, and gold, do not (see Electromotive series of the metals).

Contact of the zinc or iron with an inactive metal, like platinum, always hastens the interaction, and therefore renders the evolution of the hydrogen more conspicuous. Such an arrangement is called a *couple*, and its efficiency depends on the electric states of the two metals (see Solution tension).

When water is *not* used along with the acid, the latter is either inactive or undergoes a different sort of chemical change. Thus, dry, gaseous or liquefied hydrogen chloride hardly interacts at all with zinc. Pure, concentrated sulphuric acid, on the other hand, although almost unaffected by zinc in the cold, is violently decomposed when

heated. The action, however, is not a simple displacement (see below) of the hydrogen. The oxygen is removed from a part of the acid, and water and hydrogen sulphide are formed :

$$4Zn + 5H_2SO_4 \rightarrow 4ZnSO_4 + 4H_2O + H_2S.$$

Preparation of Hydrogen from Water. — Every one of the metals which act on dilute acids will also displace hydrogen from water, and no others will do so. Only the more active metals, like potassium and sodium, which would act with uncontrollable vigor on dilute acids, can displace the hydrogen *rapidly* from *cold* water. Magnesium and zinc show obvious action on water at 100° only, and are much assisted by contact with another metal. If any action is to be perceived in the cold, the iron, nickel, zinc, and magnesium have to be used in a state of fine powder, with great surface.

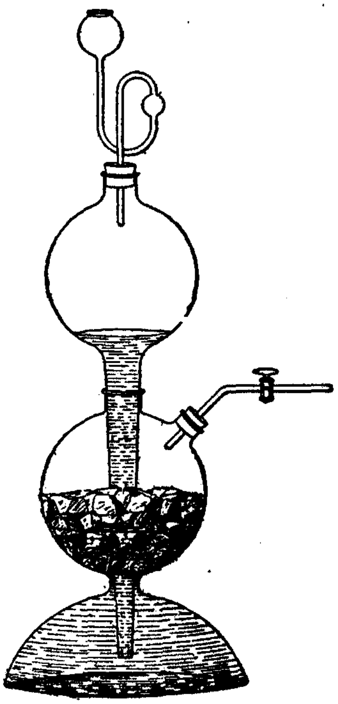


FIG. 33.

In all cases in which cold or boiling **water** is employed, the hydrogen of the water is not completely displaced. The metal forms an hydroxide, such as sodium hydroxide or magnesium hydroxide:

$$Na + H_2O \rightarrow H + NaOH,$$
$$Mg + 2H_2O \rightarrow 2H + Mg(OH)_2.$$

Sodium, which is one of the constituents of common salt, may be used to illustrate this sort of action. As it is lighter than water, it must be held under the surface by means of a piece of wire-gauze in order that the gas may be collected (Fig. 34). Most of the water serves the mechanical purpose of permitting the collection of the gas, and only a small fraction of it takes part in the change. The solution has a soapy feeling and turns litmus from red to blue. This color reaction is the precise opposite of that of acids (p. 93). Substances

causing these two effects are called *alkalies*. Evaporation of the resulting very dilute solution reveals the sodium hydroxide, the alkali, as a white solid.

With **steam** at a red heat, metals like iron, zinc, and magnesium

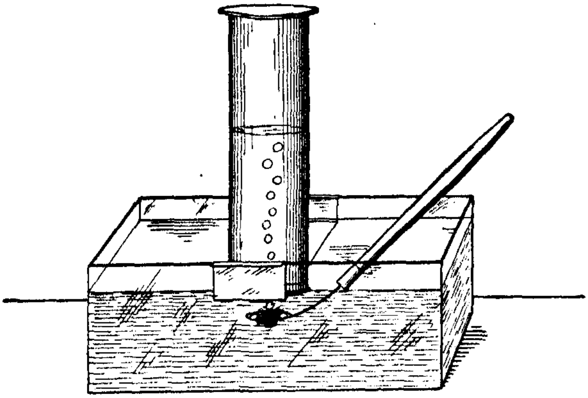


FIG. 34.

interact vigorously. The metal is placed in a tube in which it can be strongly heated (Fig. 35). The steam, generated in a flask, enters at

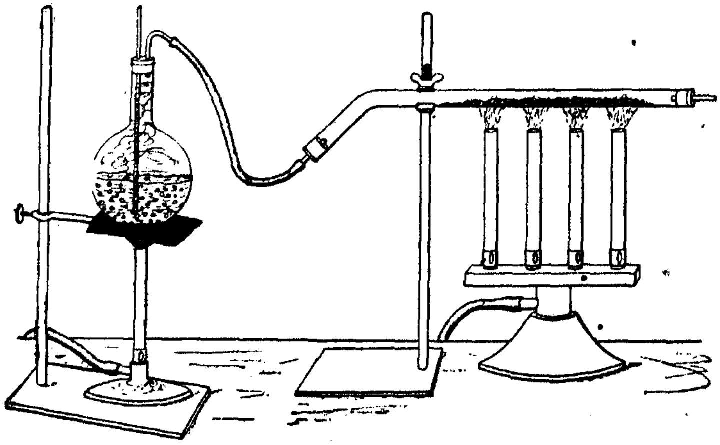


FIG. 35.

one end of the tube, and the hydrogen passes off at the other. Since, at a red heat, all hydroxides, except those of potassium and sodium,

are decomposed into an oxide of the metal and water, $Mg(OH)_2 \rightarrow MgO + H_2O$, the *oxides* are formed in this case:

$$Mg + H_2O \rightarrow MgO + 2H.$$

Iron gives the magnetic oxide, Fe_3O_4. Hence, to make the equation, four unit-weights of oxygen, and therefore four formula-weights of water, are required:

$$4H_2O + 3Fe \rightarrow Fe_3O_4 + 8H.$$

Tests.—The effect of a solution of an acid (p. 93) or an alkali (see above) upon litmus solution is an illustration of a chemical **test.** In this case a mere trace of a highly colored body dissolved in water interacts with a correspondingly minute trace of the acid or alkali under examination. Yet the product has such marked color that its presence is immediately recognizable. Tests for various kinds of materials are eagerly sought by chemists for use in identifying unknown substances. Any property which is so conspicuous as to be apparent when *very little* material is concerned will serve as a test. Thus the precipitation of calcium carbonate (p. 68) enables us to recognize the presence of carbonic acid. The test consisted in the addition of lime-water.

The Other Ways of Preparing Hydrogen.—For special purposes, hydrogen may be made by boiling an aqueous solution of sodium hydroxide with aluminium turnings, when sodium aluminate is formed: $Al + NaOH + H_2O \rightarrow NaAlO_2 + 3H$; also by heating powdered zinc and dry sodium hydroxide, the product being sodium zincate: $Zn + 2NaOH \rightarrow Na_2ZnO_2 + 2H$. It may likewise be made by electrolyzing solutions of compounds of metals which, when free, displace hydrogen from cold water. Thus electrolysis of sodium chloride or sodium hydroxide in aqueous solution liberates chlorine at the positive wire and hydrogen and sodium hydroxide (p. 97) at the negative wire (see Discharging potentials, Chap. xxxviii).

Displacement.—We now have before us illustrations of two subvarieties of the third kind (p. 15) of chemical change. In this kind, compounds are decomposed and the parts combine in a new way. The first sub-variety was *double decomposition,* as in the action of sodium chloride upon silver nitrate:

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3.$$

In this class of cases *two compounds* interact, each splits into the radicals of which it is composed, and *two new compounds* are formed by union of the radicals crosswise. The actions used in the preparation of hydrogen differ from these inasmuch as **one compound and one element interact, the compound splits into its radicals, and one compound and one free element are produced**:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H,$$
$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + 2H.$$

The former element, here the zinc, is said to **displace** the latter, here the hydrogen, from combination. In double decomposition there is an *even exchange*, the sodium, for example, giving up one radical (Cl), and getting another (NO_3), whereas in displacement one element gains a radical while another loses it, the zinc, for example, giving up nothing but getting SO_4, while the hydrogen loses SO_4, and gains nothing in return.

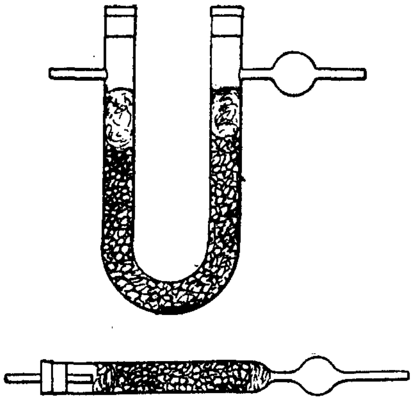


FIG. 36.

It should be noted, that although in the former of the above illustrations the Ag may be said to displace the Na from combination with the Cl, the term *displace* is used technically only when the element displaced escapes in the free condition.

Purification of Gases. — Hydrogen made in any of the above ways is impure (p. 34). As made by the first three methods, a good deal of water vapor is mixed with it. Other impurities, like hydrogen sulphide and arsine, come from the action of the acid on foreign materials in the zinc (p. 95). Some of the acid, if it is volatile, will also be taken over with the gas. When the object for which the gas is being made demands it, we must know what the impurities to be expected are, and take proper means of removing them.

Gases are freed from aqueous vapor by means of calcium chloride or concentrated sulphuric acid, which greedily absorb moisture. The

former is used in granulated form in straight or bent tubes (Fig. 36). The latter is applied by saturating pieces of pumice-stone with the acid and filling similar tubes with the fragments. Or the acid may be placed in a gas washing bottle (Fig. 37). For extremely complete drying, a tube may be filled with phosphoric anhydride sifted upon glass beads or glass wool. Forethought must be used to avoid a drying agent which will interact with gas. The longer the gas remains in contact with the drying agent, the more perfect, up to a certain limit, is the purification effected. In all cases, the stream of gas must pass slowly.

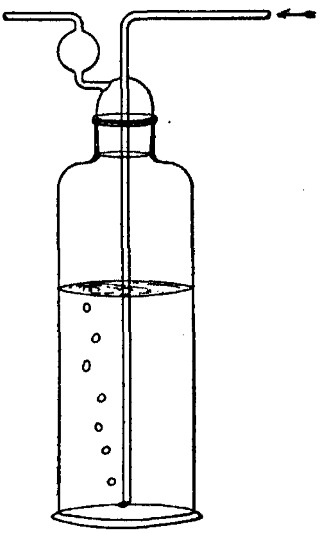


FIG. 37.

Particles of liquid or solid matter are always carried along by freshly made gases. These will pass with the gas through sulphuric acid without being affected. A plug of cotton or of glass wool in some part of the tubing is required to arrest them.

Valence. — We shall gain much help in the making of equations if we now introduce and bring into relation to the symbols a conception for which the remarks about atomic weights (p. 50) have paved the way. It will have been observed that the composition of the chlorides of aluminium, tin, and sodium are represented by the formulæ $AlCl_3$, $SnCl_2$, and NaCl respectively. Again, the hydroxide of sodium is NaOH, while those of magnesium and calcium are $Mg(OH)_2$ and $Ca(OH)_2$. In making equations we constantly need to know whether the chloride of an element, say magnesium, is MgCl, or $MgCl_2$, or $MgCl_3$, or $MgCl_4$, etc., and whether its sulphate is $MgSO_4$, or Mg_2SO_4, or some other combination of the symbols. To answer questions like this it is not necessary to know the formula of every compound of each element: the apparent disorder of these numbers can be reduced to rule, and the reader should endeavor thoroughly to master the rule before going farther.

If the method by which the atomic weights were derived from equivalents (p. 50) is now reëxamined, the nature of this rule will be

seen. It was found, for example, that 9.03 parts of aluminium (p. 50) combined with the equivalent weights of the other elements, and therefore with 35.45 parts of chlorine. If this weight of aluminium had been accepted as the final unit (the atomic weight), then it would have been represented by the symbol Al, and, since Cl stands for 35.45 parts of chlorine, the formula of the chloride would have been AlCl. In point of fact, however, a number three times as large as the equivalent, namely, 27.1, was chosen as the atomic weight of aluminium, and symbol Al stands for this triple quantity. If the equivalent of chlorine had also been tripled in making its atomic weight, the amounts represented by the symbols would still have been chemically equivalent, and the formula would still have been AlCl. But the equivalent of chlorine was left unaltered. Hence, to get the equivalent amounts (*i.e.*, the actual combining quantities) of the two elements, we must have 3Cl with 1Al. The formula is thus $AlCl_3$. Now, it is evident that this tripling of the equivalent of aluminium will affect the formulæ of *all* its compounds. Whenever it is combined with an element which, like chlorine, has identical equivalent and atomic weights, the formula of the compound will be of the form AlX_3. In accordance with this we have the bromide $AlBr_3$. In making the formulæ of compounds of aluminium, the chief thing to be kept in mind, therefore, is the fact that its atomic weight contains three equivalents and always combines with three equivalents of another element. This fact we state by saying that the **valence** of the atomic weight of aluminium is three, or simply that **the element aluminium is trivalent.**

Similarly, the equivalent of tin is 59.5 and its atomic weight is 119. This atomic weight therefore contains two equivalents of tin and combines with two equivalents of any other element. Hence, the formula of a compound of tin with an element of the chlorine class will be SnX_2. Thus tin is **bivalent.** In like manner the equivalent of sodium is 23, and this number was not altered in making the atomic weight. Hence, the symbol Na stands for one equivalent, and the formula of the compound with chlorine is NaCl. Elements whose atomic weights are identical with their equivalents are described as **univalent.**

Thus **the valence of an element** may be defined as **the number of equivalent weights contained in its atomic weight.** Arithmetically it is the integer by which the equivalent weight was multiplied in forming the atomic weight. The above explanation shows that

we may define the valence of an element also as the number of atomic weights of a univalent element, with which its atomic weight will combine. A more complete definition will be given presently.

Sometimes the valence is indicated in the symbol thus: Al^{III}, Sn^{II}, Na^{I}, Cl^{I}, Br^{I}. The table of atomic weights (p. 50) shows the following additional cases: O^{II}, Cu^{II}, S^{II}, Hg^{II}, H^{I}, Fe^{II}, Mg^{II}, C^{IV}. With the help of this list the formulæ of compounds may easily be made. Thus, oxygen is bivalent, and an atomic weight of oxygen, represented by O, will combine with two atomic weights of a univalent element as in $O^{II}H_2{}^{I}$ (water), or with one atomic weight of a bivalent element as in $O^{II}Sn^{II}$ (stannous oxide), $O^{II}Hg^{II}$ (mercuric oxide), $O^{II}Cu^{II}$ (cupric oxide), $O^{II}Mg^{II}$ (magnesium oxide). Again, carbon being quadrivalent, the atomic weight combines with four units of chlorine and of hydrogen in $C^{IV}Cl_4{}^{I}$ (carbon tetrachloride) and $C^{IV}H_4{}^{I}$ (methane); or with two units of oxygen and of sulphur in $C^{IV}O_2{}^{II}$ (carbon dioxide) and $C^{IV}S_2{}^{II}$ (carbon disulphide). When it combines with a trivalent element, equal numbers of equivalents of each element must be used, as in $C_3{}^{IV}Al_4{}^{III}$ (aluminium carbide), where C_3 and Al_4 contain twelve equivalents each. This method, with exceptions to be noted below, will give the formulæ of all compounds containing only two elements — so-called **binary compounds**.

The above mode of handling valence is based upon the notion of *combination* in equivalent proportions. Another variety of chemical change, namely *displacement* (p. 99), is often of assistance in enabling us to determine the valence of an element. It will be noted that when Al acted upon hydrochloric acid (p. 96) and combined with 3Cl, it necessarily displaced the 3H with which the 3Cl was formerly united. It was *equivalent* to 3H for the purpose of holding 3Cl in combination. It is from this aspect of the relation that the word "valence" comes. Al is *equi-valent* to 3H, and, H having the unit valence, Al is trivalent. Similarly, since one atomic weight of zinc, represented by the symbol Zn, displaces 2H (p. 95), zinc must be bivalent. Combining this with the former conception, we reach the common definition of the valence of an element: **The valence of the atomic weight of an element is the number of atomic weights of hydrogen, or of some other univalent element, which it combines with or displaces.**

Formulæ are often written so as to show the valence plainly. Thus, K—Cl indicates, by the single line, that each element is uni-

valent. Two or more lines meeting at a symbol, indicates that that element is bivalent or trivalent:

$$Al\begin{matrix} /Cl \\ -Cl, \\ \backslash Cl \end{matrix} \quad Mg\begin{matrix} /Cl \\ \backslash Cl \end{matrix}, \quad Mg{=}O, \quad O{=}Fe{-}O{-}Fe{=}O, \quad \begin{matrix} Fe{=}O \\ >O. \\ Fe{=}O \end{matrix}$$

Here Al and Fe are trivalent, Mg and O bivalent. The lines may be drawn in any direction, as the last two formulæ show. As many lines proceed from each symbol as will represent its valence. The resulting structures are called **graphic formulæ**.

The Valence of Radicals. — In the preceding section it has been seen that the valence of elements can easily be determined when they are present in binary combination. This is no longer the case when more than two elements are united together. A study of chemical changes shows, however, that even here the conception of valence can still be employed. In the interaction of zinc with dilute sulphuric acid:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H$$

the group SO_4 passes as a whole from combination with 2H to combination with Zn. Hence, although we cannot by inspection determine the valence of sulphur, we do perceive that the radical SO_4, as a whole, must be bivalent. It occurs, in fact, in all sulphates, as Ag_2SO_4, $MgSO_4$, and $Al_2(SO_4)_3$, and in the interactions of these substances it usually passes intact from one state of combination to another, and behaves as if it were a unit of a single element of valence two. Again, in the interaction of salt with silver nitrate (p. 99), we observe that the radical NO_3 is univalent. Still again, the compositions of the compounds $CaCl_2$ and $Ca(OH)_2$ show that the radical OH (hydroxyl) is univalent. The formula NaOH leads to the same conclusion.

This addition to our ideas enables us greatly to extend the list of substances of which we can write the formulæ. Thus, the hydroxides all contain $(OH)^{I}$, *e.g.* $Al^{III}(OH)_3^{I}$ (aluminium hydroxide), $Sn^{II}(OH)_2^{I}$ (stannous hydroxide), $Cu^{II}(OH)_2^{I}$ (cupric hydroxide). The nitrates all contain $(NO_3)^{I}$, as: $H^{I}(NO_3)^{I}$ (nitric acid), $Mg^{II}(NO_3)_2^{I}$ (magnesium nitrate). It is to preserve the identity of the radicals that we write them in brackets and place the factor outside, instead of using the forms AlO_3H_3, MgN_2O_6, and so forth. In fact, we regard as binary compounds, substances which commonly interact as if the radicals were single elements. In all actions in which the radicals preserve

their integrity, the conception of valence proper to binary compounds may be used for the more complex compounds also.

How to Ascertain the Valence of an Element or Radical.— The above shows that the valence of one element or radical may always be ascertained by examination of the formula of a compound containing another element or radical of known valence. Thus, when we know the formula of sodium iodide to be $Na^{I}I$, or that of hydrogen iodide to be $H^{I}I$, we infer that iodine is univalent. The formula of silica (sand) SiO_2^{II} shows silicon to be quadrivalent, and indicates that the chloride must be $SiCl_4$. Similarly the formula of calcium carbonate $Ca^{II}CO_3$ shows that the radical CO_3, which is common to all carbonates, must be bivalent. Hence, the chemist does not memorize the valences themselves; he recovers them when needed by recalling the formula of a compound containing a more familiar element or radical.

It is absolutely essential that correct valences should be used in constructing equations, and, at first, the student will find the task by no means easy. He should give special attention to this matter until, by solving the exercises at the end of this chapter, and by careful examination of all the equations encountered in the text, he has mastered the subject.

Multiple Valence and Exceptional Cases.— Some elements show more than one valence. This is as much as to say that an atomic weight of such an element may form stable compounds with two, or even more different numbers of equivalents of another element. This fact has already been mentioned, for it is implied in the law of multiple proportions (p. 41). Thus an atomic weight of tin may form two different compounds with chlorine, namely, $Sn^{II}Cl_2$ (stann*ous* chloride) and $Sn^{IV}Cl_4$ (stann*ic* chloride). Tin behaves in the same way towards other elements, however, and we have a *series* of stann*ous* compounds, SnO, $SnBr_2$, and so forth, and a corresponding series of stann*ic* compounds, SnO_2, $SnBr_4$, etc. Two different valences of the same element or radical gives rise therefore to two complete sets of compounds. The nomenclature used to distinguish the two series has been discussed before (p. 70). As a rule, an element passes from one form of combination to another without change of valence. But compounds of elements like tin can also undergo changes in course

of which the valence alters. Cases of this kind will be considered when they arise (see Preparation of chlorine).

The regular valence of an element cannot be learned by examining the composition of a compound chosen at random. Thus FeS, H_2S, HgS, and other compounds show sulphur to be bivalent. There is also a series in which sulphur is sexivalent, as in SO_3. But the compound S_2O_3, in which sulphur appears to be trivalent, is an isolated case. Again, FeO, FeS, $FeCl_2$ show iron to be bivalent, and $FeCl_3$, $Fe_2(SO_4)_3$, etc., show it to be also trivalent. But Fe_3O_4, the magnetic oxide, is an exception. Valence has to do mainly with chemical *interactions*, in which the element either passes from one state of combination to another without change of valence, or goes over into a compound of another regular series with another regular valence. It is not a matter of statics. Hence, questions as to the magnitude of the valence in isolated compounds like Fe_3O_4, N_2O, and so forth, are at present of minor importance.

A definition of valence differing from those given above is preferred by many chemists. The atomic weight of a univalent element can hold but one unit of another element in combination. Thus, the weight of chlorine represented by Cl can hold but one H or one Na in combination. An atomic weight of a bivalent element, although it combines with but one unit of another bivalent element, may hold as many as two units of a univalent element in combination. But it cannot hold more. A unit of a trivalent element, however, may hold as many as three units, provided the other element is univalent. In this point of view the **valence of an element is the maximum capacity of its atomic weight to hold atomic weights of other elements in combination.**

Valence is often defined as the power of the atomic weight of one element, to hold units of other elements in combination. But the word *power* suggests that valence is a measure of the force with which the elements are held together, whereas it has to do with the quantity of matter only. Gold is trivalent, but holds chlorine with incomparably less force than does sodium which is only univalent.

Physical Properties of Hydrogen. — Some of these may be given in tabular form:

Colorless	Crit. temp., about − 234°
Tasteless	Sp. Ht. (gas), 3.4
Odorless	Boiling-point, − 252.5°
Density (air = 1), 0.0695	Melting-point (58 mm.), − 260°
Density (H = 1), 1	Sol'ty in Aq, 1.9 vols. in 100 (14°)
Wt. of 1 l., 0.08987 g.	

Air is 14.5 times as heavy, hence the gas may be poured upwards and is used for filling balloons. A liter flask filled with air requires about 1.2 g. to be added to the tare to restore the balance when the air is dispaced by hydrogen. Its specific heat is about seventeen times that of oxygen (0.2). Its thermal conductivity is greater than that of any other gas. Hence a wire, raised to incandescence in

air by means of an electric current, cannot be kept at a red heat, even, by the same current in hydrogen.

Hydrogen was first liquefied in visible amounts by Dewar (1898). The liquid is colorless, and, when allowed to evaporate rapidly under reduced pressure, freezes to a colorless solid. All other gases except helium solidify easily when led into a vessel surrounded by liquid hydrogen.

Hydrogen is absorbed, for the most part in a purely mechanical way, by many metals. Heated iron will take up 19 times its volume of hydrogen. Under similar conditions gold takes up 46 volumes, platinum in fine powder 50 volumes, palladium 502 volumes, and silver none. The maximum absorbed by palladium under favorable conditions is 873 volumes. It is still a question whether, in the case of palladium, a part of the gas is not in combination.

Diffusion. — If a volume of gas is inclosed at one end of a cylinder, the rest of which is entirely empty, and is suddenly released from this confinement, it spreads with extreme speed so as to occupy the whole of the cylinder to an equal degree. This spreading is not an effect of gravitation, since it takes place upwards or downwards with equal celerity. The same phenomenon is observed when, in everyday life, a bottle of scent is opened. The vapor, on escaping, begins to penetrate in all directions through the room, showing its presence by its odor. The motion, as this instance shows, takes place through a space occupied by another gas more slowly than, but just as surely as, when the space is empty. The material of gases has in fact an independent power of locomotion. The resulting phenomenon we call **diffusion**. It is constant in rate for each gas under like conditions, and hydrogen has the greatest speed of diffusion of all the gases.

The interdiffusion of gases and the absence of gravity effect may be shown simultaneously. •A jar is filled with carbon dioxide and a jar of air is inverted and placed mouth to mouth with the other. After a few minutes, and in spite of the fact that carbon dioxide, measured in bulk, is one-half heavier than air, as much of each gas will be found in the cylinder of the other as in its own. Limewater (p. 68) will show the presence of carbon dioxide in the upper jar. The phenomena of diffusion must not be confused with cases like the pouring of hydrogen upward to displace air in an inverted jar. In this case the gas flows *en masse*, and the gravity effect is the very one on which we depend for the success of the experiment. It is when hydrogen scatters itself in a somewhat slower way, and downward and sideways as well as upward, that we have diffusion. The word indicates the *scattering* rather than the *flowing* nature of the phenomenon.

The different rates of diffusion of different gases are easily shown by comparing their several speeds with that of air, when both pass through a wall of unglazed, porous porcelain.

The porous cylinder *A* on the left (Fig. 38) contains air and is connected with a wide tube which dips beneath the surface of the water. When a cylinder *H* containing hydrogen is brought over it, rapid escape of gas takes place through the water, showing that a rise in pressure has taken place inside the porous vessel. Before the cylinder of hydrogen approached it, the air was moving both outwards and inwards through the porcelain, but, being the same air, the speed of motion was equal in both directions, and therefore the pressure inside was not affected. It is important to note that there was at no time rest, there was simply equal motion in both directions. When the hydrogen atmosphere surrounded the cylinder, the hydrogen gas moved more rapidly into the cylinder than the air inside could move out, and hence an excess of pressure quickly arose in the interior.

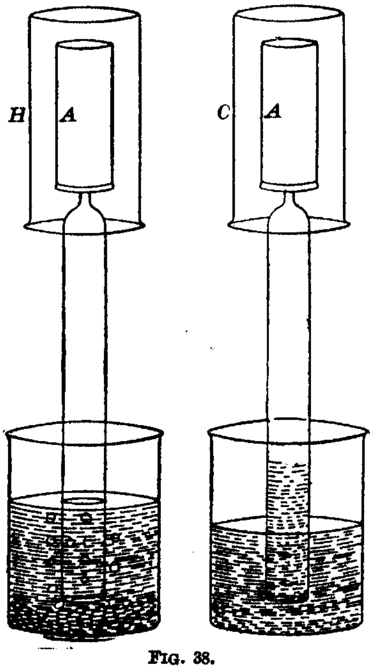


FIG. 38.

The cylinder on the right is similar, but a vessel *C* filled with carbon dioxide, a gas heavier than air (density 1.53, air = 1), surrounds it. Here the air moves out faster than the gas can move in, a reduction in pressure takes place, and the water rises.

Exact measurement shows that the lighter a gas is in bulk, the faster its parts move by diffusion in any direction. The rate is inversely proportional to the square root of the density of the gas. Thus, for hydrogen and air it is in the ratio $\sqrt{1} : \sqrt{.0695}$, or 3.8 : 1. For air and carbon dioxide it is $\sqrt{1.53} : \sqrt{1}$, or 1.24 : 1.

Chemical Properties of Hydrogen. — Hydrogen, delivered from a jet, burns in air or pure oxygen. A cold vessel held over the almost

The action of catalytic agents is itself a refutation of this blundering assumption. Putting a little platinum in a mixture of oxygen and hydrogen cannot add to the energy contained in these substances, and cannot therefore increase their intrinsic tendencies to unite. Yet in its presence an almost nonexistent action becomes suddenly explosively violent. There are other far more potent factors than affinity which determine the direction and speed of many chemical changes (see Chemical equilibrium).

In this connection, it is worth noting that, while increasing the speed of a train or a ship requires a great addition to the energy expended, and is very costly, increasing the speed of a chemical change requires the expenditure of no energy whatever. The employment of a couple (p. 96) or a catalytic agent adds nothing to the energy the separate bodies possessed before they were mixed. And the catalytic agent is recovered *unchanged* and as efficient as ever at the end. Theoretically, therefore, these agencies cost nothing. The increased speed in the formation of the products is obtained gratis. The contact method of making sulphuric acid (*q.v.*) illustrates the way in which commerce has taken advantage of this fact.

The Speed of Chemical Actions: a Means of Measuring Activity. — The speed of a chemical action is measured by the number of atomic or formula weights of the substance undergoing change in a given time. Now, one means of measuring the relative chemical activities of several substances, and, therefore, of the relative amounts of available chemical energy they contain (p. 26), is to observe the speed with which they undergo the same chemical change (p. 28). Thus we may compare the activities of the various metals by allowing them separately to interact with hydrochloric acid and collecting and measuring the hydrogen liberated per minute by each. It will be seen, even in the roughest experiment, that magnesium is thus much more active than zinc. The comparison must be made with such precautions, however, as will make it certain that the conditions under which the several metals act are all alike. Thus, in spite of the heat evolved by the action, means must be used, by suitable cooling, to keep the temperature at some fixed point during the experiment, for all actions become more rapid when the temperature rises (p. 72). Again, the pieces of the various metals must be arranged so that equal surfaces are exposed to the acid in each case; for pieces of the same metal, having, of course, the same intrinsic activity, will nevertheless give hydrogen more rapidly the larger the surface they expose. Equal weights of zinc will finally give equal weights of hydrogen; but if one of them is in the form of foil while the other is a cylinder, the former, although it will not last so long, will give much more hydrogen per minute. Still again, the portions of hydrochloric acid must contain the same percentage of hydrogen chloride in each case, for the metal

will secure the acid it needs with less delay in a more concentrated solution than in a less concentrated solution, and in the former case will therefore displace hydrogen more rapidly. When these and other precautions have been taken, a true comparison of the relative activities of the metals with respect to this particular action may be made. It is found that the order in which this comparison places the metals is much the same as that in which they are placed by a study of other similar actions. This is natural, since we are really comparing, in each case, the amount of chemical energy in each metal. A single table suffices, therefore, for all purposes. This table is given in connection with a more exact method of comparing the activities of the metals (see Electromotive series of the metals). The speed of chemical changes is discussed in greater detail under Chemical Equilibrium (see also Sulphurous acid).

Exercises. — 1. What are the valences of the negative radicals of phosphoric acid (p. 71), and of acetic acid (p. 93)? What must be the formulæ of calcium phosphate, cupric acetate, aluminium phosphate, ferrous carbonate, ferrous sulphate, cupric chloride?

2. What is the valence of phosphorus in phosphoric anhydride (p. 71)? What must be the formulæ of the chloride and the sulphide of phosphorus, and of aluminium oxide?

3. What are the valences of the elements in the following: LiH, NH_3, SeH_2, BN?

4. What are the valences of the metals and radicals in the following: $Pb(NO_3)_2$, $Ce(SO_4)_2$, KCl, $KMnO_4$ (potassium permanganate)? Name all the substances in 3 and 4.

5. Write the formulæ of ferrous and ferric oxides, of ferrous and ferric nitrates, of stannous and stannic sulphides.

6. What must be the relative rates of diffusion of hydrogen and of carbon dioxide?

7. Make equations to represent (*a*) the reduction of lead dioxide (PbO_2) by hydrogen; (*b*) the actions of aluminium upon cold water and upon steam at a red heat.

CHAPTER VIII

WATER

THE great quantity of water which occurs in nature makes it one of the most familiar chemical substances. The ocean covers about three-fourths of the surface of the earth, and in most habitable regions lakes and streams abound. Water is found also in the bodies of both animals and plants in large quantities, and is indeed essential to the working of living organisms.

Natural Waters. — The water found in nature varies greatly in the amount of foreign material which it contains. Sea-water holds about 3.6 per cent of solid matter in solution, while rain-water is the purest natural water. Even rain-water contains foreign matter, however. When we heat it, bubbles of gas form on the sides of the vessel, showing that oxygen and nitrogen from the air have been dissolved by the water as it fell. On evaporating a considerable mass of such water, we find that, aside from dust, crystals of chemical substances, such as ammonium nitrate, may be recognized in the residue. Of well and surface waters, some which contain calcium sulphate, calcium bicarbonate, and compounds of magnesium in solution are described as **hard**. Others contain compounds of iron, and still others are effervescent and give off carbon dioxide. These are called mineral waters. All of the dissolved substances are obtained by the water in its progress over or under the surface of the ground.

Water which is to be used for domestic purposes is examined, not only to ascertain the amount of the ingredients which produce hardness, but also with reference to the proportion of organic matter which it may hold in solution. This usually gains access to the water by admixture of sewage (p. 72). It is not the organic matter itself which is deleterious, but the bacteria of putrefaction and disease which are likely to accompany it. Inoculation of culture media with the water can alone show whether or not the latter are present.

Purification of Water. — The foreign materials which water may contain are divisible into two kinds, — dissolved matter and suspended

matter. No water is free from either of these varieties of impurity. In chemical laboratories distilled (p. 38) water of a more or less pure kind is always employed, but this represents only a crude purification. By using a platinum still and condenser, water of much greater purity can be obtained. Yet, on account of the solvent power of water, it is impossible to keep such a liquid even for a short time. Ordinary glass dissolves in water to a very noticeable extent.

The purity of water is most easily investigated by measurement of its resistance to the passage of electricity. A column only one millimeter long, of the purest distilled water that can be made, has a greater resistance than a copper wire of the same cross-section and long enough to reach a thousand times round the earth at the equator. During a few minutes' exposure to the air, or contact with a glass vessel, however, a sufficient amount of foreign material (p. 95) of high conductivity is taken up to diminish its resistance very greatly.

For ordinary purposes the **suspended** matter which water contains is removed by **filtration** (p. 11). In the laboratory this takes place through unsized paper. The pores of the paper are sufficiently small to retain particles of the dimensions usually met with, while permitting the passage of the water with its dissolved matter. On a large scale, beds of gravel are employed. In the household the Pasteur filter is more compact and efficient. The water is forced by its own pressure through the pores of a closed tube made of unglazed porcelain. Care must be taken to clean these tubes at frequent intervals, so that organic and perhaps putrescent matters may not accumulate upon them. If the cleansing is not carried out, the Pasteur filter-tube becomes a breeding-place for bacteria, and may add greatly to the contamination of the water instead of diminishing it.

Matter in **solution** cannot be removed by filtration, and is eliminated by **distillation**. Since the water is converted into steam and is condensed in platinum or tin pipes, only gases or volatile liquids dissolved in it can pass into the distillate.

Physical Properties of Water. — When we view a white object through a deep layer of water we find that the liquid has a blue or greenish-blue color. At a pressure of 760 mm., it exists as a liquid between 0° and 100°. Below 0° it becomes solid, above 100° a gas. Of all chemical substances it is the one which we use most, so that familiarity with its properties is indispensable to the chemist. It will serve also as a typical liquid, since it differs from others only in details.

The weight of a cubic centimeter of water at 4° gives us our unit, the gram. A kilogram of water at 0° occupies 1.00013 liters, or 0.13 c.c. more than at 4° C. A kilogram of ice at 0° occupies 1.09083 liters, or 90.7 c.c. more than an equal weight of water. The volume of the same weight of water at 100° is 1.0432 liters.

Ice. — The raising or lowering of the temperature of a gram of water through one degree corresponds to the addition or removal of one calorie of heat. The conversion, however, of a gram of water at 0° to a gram of ice at 0° requires the removal of 79 calories of heat. The mere melting of a gram of ice causes an absorption of heat to the same amount. This is called the **heat of fusion of ice**. At 0° a mixture of ice and water will remain in unchanged proportions indefinitely. Any cause which tends permanently to lower or raise the temperature by a fraction of a degree, however, will bring about the disappearance of the water or of the ice respectively. This temperature is called the **melting** or the **freezing point**. Properties of this kind, marked by **transition points** from one state to another, are much used in chemistry for keeping other bodies or systems at a constant temperature during measurement or observation. A mixture of ice and water surrounding a body, when kept in constant agitation, will automatically maintain the body at a fixed temperature (0°) so long as both components hold out.

Steam and Aqueous Tension. — At atmospheric pressure, water passes into steam rapidly at 100°, but at lower temperatures, and even when frozen, it does the same thing more slowly. The best way to define the quantity of the vapor at various temperatures is by the gaseous pressure it exercises. This is proportional to the concentration (p. 81) of the aqueous material in the space above the water, and has a definite value for each temperature. Its amount may be shown by allowing a few drops of water to ascend into the vacuum at the top of a barometric column (Fig. 39). The tube on the left shows the mercury when nothing presses on its surface. The tube on the right shows the result of admitting the water. The tension of the atmosphere being the same for both, the smaller height of mercury which now suffices to counterbalance it shows that something, which can be nothing but the water vapor, is pressing on the surface of the mercury, and makes up the rest of the total stress needed. The difference in the height of the two columns gives the value of this pressure, which we call the **vapor pressure** of the water. The jacket surrounding the tube on the right enables us, by adding ice or warm water, to

keep the water that is admitted to the vacuum, and the parts of the apparatus immediately in contact with it, at any temperature between 0° and 100°.

When ice is used outside, and a piece of it is introduced into the vacuum, the vapor it gives off quickly reaches a pressure of 4.5 mm. The vapor pressure of the ice takes the place of 4.5 mm. of mercury in balancing the atmospheric pressure, and so the mercury column falls by this amount. Similarly, water at 10° causes a fall of 9.1 mm. and at 20° of 17.4 mm., so that these represent the mercury-height values of the vapor pressure at these temperatures. The quantity of water used makes no difference, so long as a little more is present than is required to fill the available space with vapor. Of course, if a large amount is admitted, its dead weight will take the place of an equal weight of mercury in balancing the pressure of the air. If there is a measurable column of water, its height must be divided by 13.6 (the sp. gr. of mercury), and counted as if it were part of the mercury.

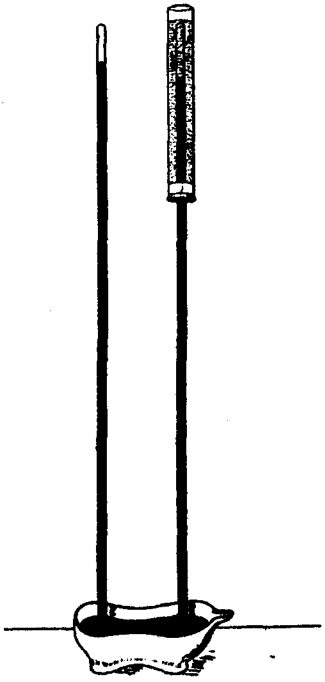


Fig. 39.

An expression is needed to describe the varying power of the water at different temperatures to maintain different pressures of its vapor. This we call the **aqueous tension** of the liquid. Its magnitude at any given temperature is measured by the maximum pressure reached by the vapor (see Kinetic-molecular hypothesis applied to liquids).

With water at higher temperatures the fall of the mercury column becomes much greater. At 50° it is 92 mm., at 70° it is 233.3 mm., at 90° it is 525.5 mm., and at 100° it is 760 mm. At the boiling-point, therefore, the aqueous tension takes the place of the whole barometric column, and is equal to the average air pressure. At 121° the aqueous tension is two atmospheres, at 180° it is ten atmospheres.

There is another standpoint from which these phenomena may be

viewed. Water vapor can exist at 10° only if the pressure upon it is 9.1 mm. or less. If we imagine the water placed in a cylinder closed by a frictionless, weightless piston (Fig. 40), then at 10° the piston will remain at rest whether we place it high or low, provided it is loaded with a weight exactly equal to that of a layer of mercury 9.1 mm. thick covering its whole area. We speak of such a system as being in **equilibrium**.* With a less weight the piston will move slowly upwards, as the vapor continually given off by the water presses upon it, until it reaches the top or the water all evaporates. Conversely, if it bears a greater load, it will move down and the vapor will condense on the walls and bottom of the cylinder until the piston comes in contact with the water itself and the vapor is all abolished. These conceptions will find constant application not only to physical but also to chemical phenomena (see Kinetic-molecular hypothesis). The expression:

$$\text{Aq. (liq.)} \rightleftarrows \text{Aq. (vap.)}$$

is used to represent the state of equilibrium in a system like the above.

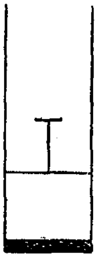


Fig. 40.

One other phase of this subject is recognized by special phraseology. When water at a certain temperature has given the full amount of water vapor to the space above it that its aqueous tension permits, we say that the space is **saturated** with vapor. That concentration of vapor which constitutes saturation varies with the temperature of the water and depends therefore solely on the power of the water to give off vapor. It has nothing to do with the size of the space, and is even independent of other gases the space may already contain (p. 88).

The space immediately above the surface of the ground, which is mainly occupied by atmospheric air, is, on an average, less than two-thirds saturated with water vapor. That is to say, such air, when inclosed in a vessel containing water, will take up about one-half more than it already contains. At 100° the water vapor displaces the air entirely, and the liquid is said to boil.

The water present in the air plays an important part in many chemical phenomena, as we shall see. All our substances and apparatus have traces of water condensed on their surfaces. This water is, in a sense, in an abnormal condition, for it does not evaporate even in

* In chemistry we do not speak of stable, unstable, and indifferent equilibrium, as is done in physics, but only of the first. The term "metastable," however, is employed (see Chap. x).

dry air. It is observed to pass off in vapor, however, when we have occasion to heat any material.

In passing into vapor, water absorbs heat without changing its temperature. A gram of water at 100°, for example, in turning into a gram of steam at 100°, takes up 537 calories. This is called its **heat of vaporization**. Steam, in fact, contains much more internal energy than an equal weight of water at the same temperature, just as water, in turn, contains more energy than ice.

The temperature of 100° is, like the melting-point of ice, an important transition point, and has the same properties, *mutatis mutandis*, as the latter. It is less exactly recoverable by simply keeping a vessel full of water in ebullition, however, because variations in the pressure of the atmosphere affect it more markedly than they do the melting-point of ice. Near to 100°, the boiling-point rises or falls about 0.037° for 1 mm. change in pressure (*cf.* p. 116). On the top of Mont Blanc water boils at 84°.

Water as a Solvent. — One of those physical properties of water which are most used in chemical work is its tendency to dissolve many substances. This subject is so important and extensive that we shall presently devote a complete chapter to some of its simpler and more familiar aspects.

Chemical Properties of Water. — Water is so very frequently used in chemical experiments in which it is a mere mechanical adjunct, that the beginner has difficulty in distinguishing the cases in which it has itself taken part in the chemical interaction. The rather limited list of kinds of chemical activity it can show should therefore receive careful notice: It (1) is a relatively stable substance. It (2) combines directly with many substances. In the commoner of the two kinds of this action, the formation of hydrates (see below), the compound exists in the solid form only, however, and is decomposed in solution. Finally, it (3) interacts with some substances in a way which we describe as hydrolysis. We shall not discuss this last property until some substance which is markedly affected is encountered (see Preparation of hydrogen chloride).

Perhaps we should add that steam at a high temperature oxidizes elements which readily combine with oxygen. For example, it turns iron into the magnetic oxide (p. 99). At such high temperatures, however, the water is partially resolved into a mixture of hydrogen and

oxygen, and, the latter being the more active of the two elements, the oxidizing effects predominate. Even other compounds containing oxygen will give exactly the same results. Hence this cannot be regarded as a property of water itself.

Water a Stable Compound. — Whether the substance is relatively **stable** or **unstable** is, in the case of a compound, the first chemical property to be given. Usually the specification is in terms of the temperature required to decompose it. Thus, potassium chlorate gives off oxygen at a low red heat. Water, even at 2500°, is but little decomposed, and reunion occurs as soon as the temperature is lowered.

Union of Water with Oxides. — When sodium combines with oxygen under certain conditions we obtain sodium oxide (Na_2O). The product unites violently with water to form sodium hydroxide:

$$Na_2O + H_2O \rightarrow 2NaOH.$$

The slaking of quicklime is a more familiar action of the same kind:

$$CaO + H_2O \rightarrow Ca(OH)_2.$$

No other products are formed. The clouds of steam produced in the second instance are due to evaporation of a part of the water by the heat produced in the formation of calcium hydroxide. The aqueous solutions of these two products have a soapy feeling, and turn red litmus blue, and the substances therefore belong to the class of alkalies (p. 98) or **bases**. Very many hydroxides which are of the same nature, for example ferric hydroxide ($Fe(OH)_3$) and tin hydroxide ($Sn(OH)_2$), are formed so slowly by direct union of the oxide and water that they are always prepared in other ways.

Some oxides, although they unite with water, give products of an entirely different character. Phosphoric anhydride and sulphur dioxide (p. 71) are of this class and yield acids.

These two classes of final products are so different that we make the distinction the basis of classification of the elements present in the original oxides. The elements, like sodium and iron, whose oxides give bases, are called **metals**; those, like phosphorus, whose oxides give acids, are called **non-metals**. The distinguishing words are selected because the division corresponds, in a general way at least, with the separation into two sets to which merely physical examination of the elementary substances would lead.

Formerly the hydroxides of met... ... ...ydrates," and the word is still used familiarly by chemists in a few cases, such as potassium "hydrate" (KOH) and sodium "hydrate" (NaOH). These substances, however, have nothing in common with the compounds properly known as hydrates whose nature is discussed in the next section.

Hydrates. — Many substances when dissolved in water and recovered by spontaneous evaporation of the solvent are found to have entered into combination with the liquid. The products, which are solids, are called **hydrates**. These compounds show definite chemical composition expressible in terms of chemical unit weights of the constituents. Often much heat is given out in their formation. Thus, in the case of washing soda, the decahydrate of sodium carbonate ($Na_2CO_3, 10H_2O$), the heat of the union (p. 76) is 8800 cal. The hydrates have physical properties entirely different from those of their components. Thus, cupric sulphate, often called anhydrous cupric sulphate to distinguish it from the compound with water, is a white substance crystallizing in shining, colorless, needle-like prisms. The pentahydrate (blue-stone or blue vitriol) is blue in color, and forms larger but much less symmetrical (asymmetric or triclinic) crystals (Fig. 41):

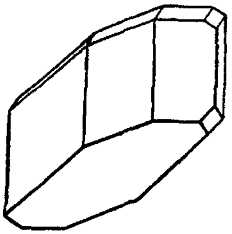


FIG. 41.

$$CuSO_4 + 5H_2O \rightarrow CuSO_4, 5H_2O.$$

When heated, the hydrates, as a rule, lose none of the constituents of the original compound, but only those of the water. They do so, in general, rather easily. Hence, to avoid the disguise of the fundamental substance which would occur if we wrote, for example, $H_{10}CuSO_9$, we segregate (as above) the elements of the water in the formula. The aqueous solutions made from the anhydrous substances and from the hydrates have identical physical and chemical properties. Hence the cheaper of the two forms is generally purchased, and many of the chemicals used in laboratories are in the form of hydrates.

Some of these hydrates decompose very readily.* The decahydrate of sodium sulphate, $Na_2SO_4, 10H_2O$ (Glauber's salt), gives up all the water it contains when simply kept in an open vessel. At 100° blue vitriol very quickly loses $4H_2O$ and the rest of the water more slowly. The last equation might therefore have been written to show a reversible

action (p. 64). A decomposition which proceeds at high temperatures, while at lower temperatures recombination of the constituents can take place, as with these hydrates, is called a **dissociation.** The decomposition of potassium chlorate (p. 64) is not a dissociation because it is not reversible; oxygen will not under any circumstances reunite with potassium chloride.

The condition which controls such actions is not, however, the temperature alone. When Glauber's salt is kept in a *closed* bottle, a very little of it loses water, and then the decomposition ceases. When the bottle is left open, the dissociation proceeds until no decahydrate remains. The cause of this we discover when a crystal of the hydrate is placed above mercury, like the ice or water in Fig. 39 (p. 116). *It shows a definite aqueous tension.* At 9° the value of this is 5.5 mm. As its temperature is raised, the tension increases. When the temperature is lowered, on the other hand, the tension diminishes, the mercury rises, and more of the water enters into combination again. Different hydrates show different aqueous tensions at the same temperature. For example, at 30°, water itself is 31.5 mm., strontium chloride ($SrCl_2, 6H_2O$) 11.5 mm., cupric sulphate ($CuSO_4, 5H_2O$) 12.5 mm., barium chloride ($BaCl_2, 2H_2O$) 4 mm.

It appears, therefore, that the water in these compounds evaporates as do ordinary waters. Those which, like washing soda, have a vapor tension approaching that of water itself, lose their water at ordinary temperatures at a rapid pace. In this connection we have to remember that atmospheric air is usually less than two-thirds saturated with water vapor, and the partial pressure of this vapor opposes the dissociation. Thus at 9°, the vapor tension of water being 8.6 mm., the average vapor pressure of water in the atmosphere will be about 5 mm. Any hydrate with a greater aqueous tension than 5 mm., at 9°, such as Glauber's salt, will therefore decompose spontaneously in an open vessel. But those with a lower vapor tension, such as the pentahydrate of cupric sulphate with a tension of 2 mm. at 9°, will not do so (see p. 135).

The behavior of hydrates does not indicate, as might seem at first sight to be the case, that the water is contained in them in some way in the free state. The fact is that the above statements, with corresponding changes in the wording, might be made of all dissociations in chemistry. Oxides give a different pressure of oxygen at each temperature, carbonates of carbon dioxide, and so forth.

The measurement of the vapor tension of hydrates gives definite information in regard to whether there are other hydrates, say of cupric sulphate, with less

than the normal number of formula-weights of water. If there were only two substances, $CuSO_4$ and $CuSO_4, 5H_2O$, with no compound of intermediate composition, then a partially decomposed specimen would be made up partly of the one substance and partly of the other. But if there were an intermediate compound, say $CuSO_4, 3H_2O$, then desiccating a specimen of the pentahydrate would give nothing but mixtures of $CuSO_4, 3H_2O$ and $CuSO_4, 5H_2O$ until all the latter was decomposed. Then, and only then, the trihydrate would begin to lose water. Now the trihydrate, being a definite and different substance, would have a vapor tension of its own, and experimental study would show its presence.

Experiment shows that there really are several hydrated cupric sulphates. The pentahydrate, at 50°, has a vapor tension of 47 mm., and this vapor tension is observed so long as any pentahydrate remains to be decomposed. As soon as the proportion of water goes down to $CuSO_4, 3H_2O$, the vapor tension suddenly drops to 30 mm. As the desiccation continues, this tension is maintained until the composition has reached $CuSO_4, H_2O$. At this point the vapor pressure falls to that of the monohydrate, 4.5 mm., and remains at this value until all the rest of the water has been removed. Had there been no intermediate compound with $3H_2O$ the tension would have dropped at once from 47 mm. to 4.5 mm. If, conversely, we try to combine water as vapor with anhydrous cupric sulphate, at 50°, a vapor pressure of at least 4.5 mm. is required to cause union to take place. The union stops when one formula-weight of water has undergone combination. To introduce more, the concentration of the water vapor must be increased to nearly seven times its first value, namely, to 30 mm. pressure. This enforces combination up to $CuSO_4, 3H_2O$. For further hydration, a still higher pressure of water vapor is needed (47 mm.), and the absorption ceases when $CuSO_4, 5H_2O$ has been formed.

There are thus three distinct reversible actions which succeed one another as the hydration proceeds:

$$CuSO_4 + H_2O \rightleftarrows CuSO_4, H_2O$$
$$CuSO_4, H_2O + 2H_2O \rightleftarrows CuSO_4, 3H_2O$$
$$CuSO_4, 3H_2O + 2H_2O \rightleftarrows CuSO_4, 5H_2O.$$

The first represents a greater affinity than the second, and the second than the third.

The graphic representation of these facts (Fig. 42) will make the behavior of the compounds clearer. The proportion of water combined with one formula-weight of cupric sulphate is laid off along the horizontal axis. The pressures at which it enters or leaves the compounds at 50° are the ordinates. As far as $1H_2O$ the pressure is constant (4.5 mm.). Beyond that point and up to $3H_2O$ it is constant but much higher. Between $3H_2O$ and $5H_2O$ it is constant again but higher still.

The tension of free water at the same temperature is 92 mm. It is constant irrespective of the amount of water, and would therefore be on a single continuous line parallel to the horizontal axis and twice as high above it as the uppermost one in the diagram. If, at 50°, a vessel of water were put under a bell jar alongside of anhydrous cupric sulphate, its vapor would be more than sufficiently concentrated fully to hydrate the compound. Again, while 4.5 mm. pressure of water vapor will cause water to combine with anhydrous cupric sulphate at 50°, a pressure of 92 mm. will be required to liquefy the water vapor at the same temperature.

The above discussion shows that the last formula-weight of water, in hydrates

which dissociate by stages, is not different in kind from the others. It differs only in the degree of tenacity with which it is held. It is therefore unnecessary, merely on this account, to dignify it by the separate name of *water of constitution*, as has been done by some chemists.

Water of hydration is frequently called **water of crystallization**, on account of the fact that when water is driven off by heating, the substance usually crumbles to pieces (**effloresces**). The term is not particularly appropriate for several reasons. It suggests that water and crystallization are related in some way, which is not the case. Sulphur, galena, potassium chlorate, and thousands of other crystallized substances, do not contain the elements of water. Nor do the substances which combine with water remain amorphous in its absence. They all crystallize from the molten condition or from some non-aqueous solvent, although, as substances different from the hydrates, their crystalline form is different. Iceland spar, or any other crystallized carbonate which can be decomposed by heating, becomes opaque and porous or falls to powder when the carbon dioxide is driven out. But it has not occurred to any one to call this carbon dioxide of crystallization! The fact is that all pure chemical substances, in solid form, when in a stable physical condition, are crystalline. Amorphous substances are always supercooled liquids.

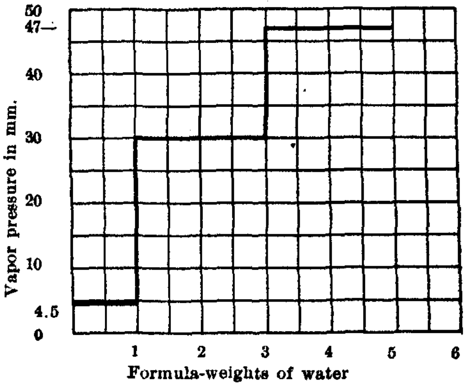


FIG. 42.

The term arose from a misconception, and, when used, always succeeds in transmitting the misconception along with the name. The ease with which some of the hydrates decomposed suggested the idea that they contained water as a *discrete substance*. There is no more justification for this idea, however, than for the notion that carbonates contain ready-made carbon dioxide. The hydrates contain the elements of water just as sugar and alcohol do, and there is no evidence that they "contain water" in any other sense than that in which the phrase might be used of these organic bodies.

In consequence of their decomposition into and formation from substances capable of separate existence, the hydrates are classed with molecular compounds (*q.v.*). The behavior of the compounds of salts with ammonia (like $2AgCl, 3NH_3$), with nitric oxide, and with each other (double salts), is quite similar.

Composition of Water.—The measurement of the proportions by weight and volume in which hydrogen and oxygen combine to form water has been the subject of a larger number of elaborate investigations than any other single problem of this kind. The difficulty in

making the former measurement arises from the fact that both constituents are gases, and therefore difficult to weigh.

The determination of this proportion which, until very recently, held its place in all chemical works, was that made by the French chemist, Dumas. His experiments gave the ratio of hydrogen to oxygen 2 : 15.96.

It was not until 1887 that Keiser obtained a figure for the oxygen appreciably smaller than this, and soon determinations by other observers showed that Dumas' proportion was probably too large. The investigation which finally settled this question was that of Edward Morley. The most striking of his experiments consisted in a series of syntheses of water, in which he weighed the hydrogen as well as the oxygen, and afterwards weighed the water produced from them. The hydrogen was confined by absorption in palladium (p. 107), and could thus be contained in large quantity in a small, elongated bulb. During the progress of the experiment it was driven out by a suitable heating arrangement. The oxygen was contained in large globes holding 15–20 liters. The losses in weight of the palladium tube and of the globes gave the hydrogen and oxygen consumed. The manipulator in which the gases were combined and the water collected is represented in Fig. 43. The gases entered through two small tubes marked *A*. Just above them, between two platinum wires, a discharge of electricity started the union and when necessary maintained it. The vessel was first filled by admitting oxygen, and the hydrogen was burned at the mouth of the tube from which it issued. This part of the apparatus was immersed in a vessel of water with transparent walls through which the union could be watched, and the steam formed was condensed and collected in the bottom of the vessel. The vacuum thus produced enabled the oxygen continually to flow into the manipulator from the globes. In this way forty-two liters of hydrogen and twenty-one liters of oxygen could be combined in about an hour and a half.

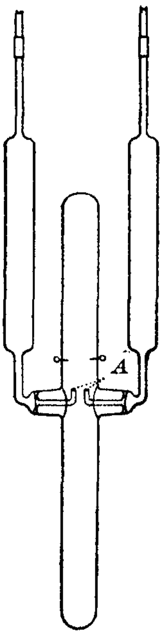


FIG. 43.

At the end of the experiment this part of the apparatus was disconnected and placed in a freezing mixture which converted the water into ice and practically condensed the whole of its vapor. The uncombined gas in the apparatus was withdrawn and its nature and quantity determined. The increase in weight of the manipulator gave the quantity of water formed. The success of each experiment could be tested by comparing the sum of the weights of oxygen and hydrogen with that of the water obtained from them. The manipulation was so skilful, and the various corrections used were so adequate, that this difference was almost negligible. The ratio of hydrogen to oxygen in water in this series of experiments was 2 : 15.879, a result which agreed with the other methods of determining the same ratio which Morley used. It agrees also exactly with the average of the numbers obtained by several other observers.

The most probable value of the ratio by weight, taking his own

and other trustworthy measurements into account, is given by Morley as 2 : 15.879 or 2.015 : 16. The proportion by volume is 2.0027 volumes of hydrogen to 1 volume of oxygen.

That the proportion by volume is very close to 2 : 1 may easily be shown. We may use a U-shaped tube closed at one end by a stopcock and graduated (Fig. 44). At first, the left limb of the tube, called a eudiometer, is filled with mercury. One of the gases is admitted so as to fill a portion of the tube and, the levels having been equalized (*cf.* p. 82), the volume of the gas is read. Then some of the other gas is introduced and the leveling and reading repeated. Let us suppose that 15 c.c. of hydrogen and 10 c.c. of oxygen have thus been taken. The right limb is then filled with mercury and closed firmly with the thumb. A spark from an induction coil passing between the two short platinum wires near the top of the tube explodes the mixture. The steam produced by the union condenses almost immediately and occupies practically no volume worth considering. When the thumb is removed, the mercury rises on the left and fills up the space left by the disappearance of part of the gases. Unless the proportion taken happens to have been exact, some of one or other of the gases will remain. Its volume is measured by equalizing the levels and reading as before. In the case we have imagined, the residual gas is oxygen, and there are almost exactly 2.5 c.c. of it. It is evident, therefore, that 15 c.c. of hydrogen united with 7.5 c.c. of oxygen; in other words, the proportion by volume is 2 : 1.

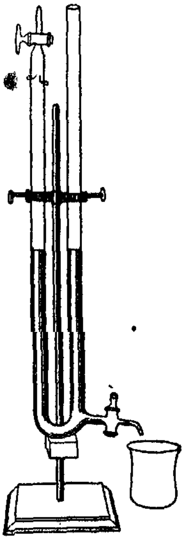


FIG. 44.

Gay-Lussac's Law of Combining Volumes. — The almost mathematical exactness with which small integers express this proportion is not a mere coincidence. **Whenever gases unite, or gaseous products are formed, the proportion by volume** (measured at the same temperature and pressure) **of all the gaseous bodies concerned can be represented very accurately by ratios of small integers.** **This** is called **Gay-Lussac's law of combining volumes** (1808). Thus, when the above experiment is carried out at 100°, in order that the product, water, may be gaseous also, it is found that the three volumes of the

constituents give almost exactly two volumes of steam. For example, 15 c.c. of hydrogen and 7.5 c.c of oxygen give 15 c.c. of steam. *Of course the hydrogen, oxygen, and steam must be measured at* the same pressure, and the temperature must remain constant (100°) during the experiment. Proper manipulation secures the former, and a jacket filled with steam (Fig. 45) the latter condition. Strips of paper, 1, 2, and 3, are pasted on the jacket in such a way that equal lengths of the eudiometer, in this case a straight one, are laid off. The three divisions having been filled with a mixture of hydrogen and oxygen in the proper proportions, the gas, after the explosion, shrinks so as to occupy, at the same pressure, only two of them.

From this universal truth in regard to the combination of gases, we draw the important inference that **the chemical unit-weights of simple substances**, and the formula-weights of compounds, **in the gaseous condition, occupy at the same temperature and pressure volumes which are equal or stand to one another in the ratio of small integers** (see Molar weights).

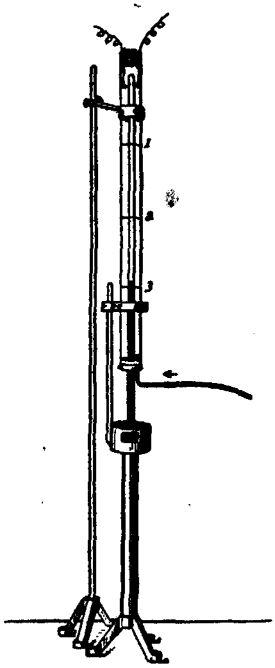


Fig. 45.

The chemical behavior of the other compound of hydrogen and oxygen, hydrogen peroxide (*q.v.*), is difficult to comprehend until further experience has been gained. Then, too, its formula (H_2O_2) cannot be justified until the means of determining molar weights in solution have been discussed. In view of these facts, and because it furnishes the simplest illustration of the meaning of a structural formula, a conception which would be quite out of place at this stage, it will be taken up later.

Exercises. — 1. Name some other transitions from one physical state to another which are familiar (p. 115).

2. What evidence is there in the common behavior of ether, alcohol, and chloroform tending to show that these liquids have high vapor tensions?

3. If the pressure of the steam in a boiler is ten atmospheres, at what temperature is the water boiling (p. 116)?

4. How many grams of water could be heated from 20° to 100° by the heat required to melt 1 kgm. of ice at 0°?

5. What do you infer from the fact that alum and washing soda lose their water of crystallization when left in open vessels, while gypsum does not (p. 121)?

6. Which facts show conclusively that hydrates are true chemical compounds? Is there any fact which throws doubt on this conclusion?

7. In what way does a hydrate differ from (*a*) a solution, (*b*) an hydroxide?

8. Should you expect to find any difference, in respect to chemical activity, between the three forms of water (ice, water, and steam)? If so, arrange them in the order of probable increasing activity (pp. 26–28). Have we had any experimental confirmation, or the reverse, of this conclusion?

9. Which contains more chemical energy, and is therefore more active, the anhydrous substance, or the corresponding hydrate?

CHAPTER IX

THE KINETIC-MOLECULAR HYPOTHESIS

As soon as we have constructed a law (p. 7) we desire immediately to find out the basis of the constant mode of behavior it epitomizes. If no explanation, that is, more detailed description, is forthcoming as the result of closer observation, we proceed to *imagine* one (p. 10). This always takes a mechanical form, often crude at first, and later undergoing refinement. Thus, at first, the phenomena of light were explained by the conception of clouds of fine corpuscles emanating from the luminous body. The chances of hitting upon an objective reality by guess-work like this is obviously remote. Whether such particles did really fly about was not the main question, however. Their value lay in the fact that they could be pictured concretely and gave a basis for further thought and perhaps suggestions for new experiments. Such a structure of the imagination is called an **hypothesis**. If it furnishes an explanation of more than one law, so much the better.

The Molecular Hypothesis. — The only mechanical basis we can imagine to account for the physical properties of matter is a discontinuous structure of some description. The fact that all kinds of matter can be compressed (gases to an enormous extent, solids and liquids to a measurable extent) may be explained, either by a diminution in the volume of the material itself, or by the closer packing together of the particles into which this material is divided. It is evident that the latter is much more in harmony with our experience. Compression, we imagine, therefore, does not diminish the actual volume occupied by matter, but crowds the particles closer together and diminishes the space between them. The same hypothesis will furnish a concrete description of how one kind of matter will frequently absorb a large quantity of another. Thus we picture the hydrogen gas taken up by iron and other metals as being packed away in the spaces between the particles of the metal. So also, in solution, the volume of the liquid does not usually increase by an amount equal to that of the substances

dissolved. Hence we imagine the particles as possibly incompressible and the interstices between them as furnishing a part of the accommodation for the foreign material. A *particle* is a fragment of matter which can be seen and measured directly, and handled separately. Since the particles of this hypothesis have none of these qualities, we distinguish them by the name **molecules. Molecules are the imaginary units of which bodies are aggregates.**

Since the behavior of gases has been considered most fully in the preceding chapters, and is in any case capable of more exact and simple description than that of solids or liquids, we shall apply this hypothesis first to them.

Kinetic-Molecular Hypothesis Applied to Gases. — Let us first build up our hypothesis to fit the *qualitative* properties of gases. The most remarkable thing about a gas, considering the looseness with which its material is packed, is the total *absence* in it of any tendency to *settling* or subsidence. Since the molecules cannot be at rest upon one another, as the great *compressibility* shows, we are driven to suppose that they are **widely separated from one another**, and that they occupy the space by constantly moving about in all directions. But a moving aggregate of particles which does not even finally settle must be in perpetual motion. We must, therefore, imagine the molecules to be wholly unlike particles of matter in having **perfect elasticity**, in consequence of which they undergo no loss of energy after a collision. They must continually strike the walls of the vessel and one another and rebound, yet without loss of motion. The *diffusibility* of gases and their mutual *permeability* require no additional assumptions. The fact that each gas is *homogeneous*, efforts to sift out lighter or heavier samples having failed, requires the supposition that **all the molecules** of a pure gas are **closely alike**.

Passing now to *Boyle's law* (p. 84), the thing to be accounted for is that when a sample of a gas diminishes in volume, its pressure increases in the same proportion. Let the diagram (Fig. 46) represent a cylinder with a movable piston, upon which weights may be placed to resist the pressure. Now the pressure exercised by the gas cannot be like the pressure of the hand upon a table, since we have just assumed that the particles are not even approximately at rest, and the spaces between them are enormous compared with the size of the molecules themselves. The gaseous pressure must therefore be attributed to the colossal hailstorm which their innumerable impacts upon

the piston produce. If this is the case, the compressing of a gas must consist simply in moving the partition downwards so that the particles as they fly about are gradually restricted to a smaller and smaller space. Their paths become on an average shorter and shorter. Their impacts upon the wall become more and more frequent. So the pressure which this occasions becomes greater and greater, and is proportional to the degree of crowding of the molecules. There are two other points which must be added. When we diminish the volume to one-half, we find from experience that the pressure becomes exactly, or almost exactly, twice as great. This must mean that although the particles are becoming crowded they do not interfere with one another's motion, excepting of course where actual collision causes a rebound. Only in the absence of interference would doubling the number of particles per unit of volume give exactly double the number of impacts on the walls. Hence the particles must have practically no tendency to cohesion. Again, the molecules must move in straight lines, because, if they moved in orbits of some kind, many of the orbits would not be intersected by the wall of the vessel until great reduction in the volume had taken place, and thus, as the volume diminished, the frequency of the impacts, and therefore the pressure, would increase faster than the concentration.

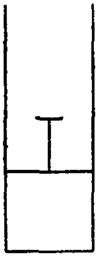


FIG. 46.

Boyle's law therefore adds four more conceptions to our molecular hypothesis, namely, that the **impacts of the particles** produce the *pressure*, that the **crowding of the molecules** represents the *concentration* (p. 80), and that the particles **move in straight lines** and **show almost no cohesion**, since *pressure* and *concentration are very closely proportional to one another.*

It will be seen, on consideration, that if the molecules are assumed to repel one another, they would do so more violently the more closely they were packed together. This assumption would therefore suit the case of a gaseous body in which the pressures increased according to some power of the concentration other than the first, and therefore much more rapidly than in known gases. In spite of its inapplicability, this notion is supposed by many people to be part of the kinetic hypothesis.

Charles' law (p. 87), that a gas receives equal increments in volume or pressure for equal elevations in temperature, requires but one addition to the hypothesis. Concretely, if our specimen of gas (Fig. 46) is at 0°, and we permit its pressure to remain constant by leaving the

same weight on the piston, then when the temperature of the gas is raised to 1°, the volume will gain $\frac{1}{273}$ of the original volume. If, on the other hand, we restrict the gas to the original volume, the pressure will evidently increase, and the augmentation will be $\frac{1}{273}$ of the original pressure. Now, how can we account for an increase in pressure as the result of heating a mass of rapidly moving molecules? The action of a particle colliding with a surface is measured in physics in terms of its mass and its velocity. It is evident that *heating* a cloud of molecules would not increase the mass of each, and it must therefore **increase the velocity of each** since the kinetic energy of all becomes greater. This conclusion is in harmony with our experience that violently rubbing a solid raises its temperature, and such a mode of treatment might plausibly be supposed to communicate motion to the minute parts of the body.

The fact that the *combining volumes of gaseous substances are equal, or stand to one another in the ratio of small whole numbers* (*cf.* Gay-Lussac's law, pp. 125–126), suggests two ideas: First, that chemical combination, considered in detail, and arranged to harmonize with this hypothesis, would involve **unions of** a few **particles** of more than one kind to form **composite molecules.*** And, second, that a simple integral relation must be assumed to exist between the **numbers of molecules in equal volumes of different gases**, at the same temperature and pressure. Avogadro (1811), the professor of physics in Turin, put forward the hypothesis that these numbers **might be equal**. A more strict study of the assumptions we have been making, and of some additional facts, has since shown that no other conjecture than Avogadro's would be consistent with them. Thus it now bears the relation of a logical deduction from the kinetic-molecular hypothesis and the properties of gases, and is known as **Avogadro's hypothesis**. It may also be put in the form: **At the same temperature and pressure, the molecular concentration** (*cf.* p. 80) **of all kinds of gases has the same value**.

The law of diffusion (p. 108) harmonizes with the kinetic-molecular hypothesis without further modification of the latter. The strict deduction of this law, as well as of the preceding ones, from our series of assumptions, will be found in any work on physical chemistry.

Finally, we have referred (p. 85) to the fact that at *low pressures*

* This is essentially the idea used by Dalton, before Gay-Lussac's law was known, however, for the explanation of the laws of chemical combination. He called it the atomic hypothesis (*q.v.*).

the concentration increases more, and at high pressures much less than Boyle's law indicates. The former effect is brought into accord with our hypothesis when we remember that the matter even of gases can cohere, as is shown plainly when they are solidified. The tendency of the molecules to cohere must therefore show itself in the gaseous condition by pulling the gas together and producing somewhat greater concentration than is strictly consistent with the value of the pressure. Although this effect of cohesion is usually insignificant, the modern method of liquefying gases (*q.v.*) depends upon it almost entirely.

The abnormally small reductions in volume which occur when the volume of the gas has already been greatly reduced remind us that, according to our hypothesis, it is only the space **between** the molecules that is diminished as pressure rises, and not the space **occupied by** the molecules. Hence, when the molecules have become so crowded together that this irreducible space begins to form an appreciable fraction of the whole, a doubling of the pressure will diminish to one-half its value only **a part** (the vacant part) of the volume the gas occupies.

If the incompressible space occupied by the molecules is called b, and that of the whole gas v, then the amended form of Boyle's law reads $p\ (v-b) = \text{constant}$. Similarly, if the cohesive tendency is taken into account, it is plain that its effect will be numerically greater at small volumes, although not so easily observed. It is in fact inversely proportional to the square of the volume. If it is expressed in the same units as the pressure by a, the total of the compressing tendencies becomes $p + \frac{a}{v^2}$. Hence Boyle's law, for constant temperatures, as amended by Van der Waals, reads $\left(p + \frac{a}{v^2}\right)(v - b) = \text{constant}$, a formula which describes the actual behavior of most gases with remarkable accuracy. Hydrogen alone, at ordinary temperatures, shows no excessive compressibility at low pressures. The cohesion (a) is so slight that the effect of the constant (b) counterbalances it from the very first.

We may summarize the facts about gases, appearing in italics above, with the corresponding fictions, in heavy type, which we have added one by one in manufacturing our hypothesis, as follows :

Facts.	Hypothesis.
Non-settling Compressibility Diffusibility Permeability	**The fictitious particles called molecules are, at 0° and 760 mm., at great average distances from one another; they are in constant motion and have perfect elasticity.**
Homogeneity	**The molecules of the same substance are closely alike.**

FACTS.	HYPOTHESIS.
Relation of pressure and concentration (Boyle's law).	The effect of pressure is produced by the impacts of the molecules, and is proportional to the degree to which they are crowded together; the molecules move in straight lines, and have almost no tendency to cohesion.
Relation of volume (or pressure) and temperature (Charles' law).	A rise in temperature increases the velocity and therefore the kinetic energy of the molecules.
Relation of atomic weights and volumes (Gay-Lussac's law).	Chemical union consists in fusion of different kinds of molecules (Dalton's hypothesis), of which there are equal numbers in equal volumes of different gases at the same temperature and pressure (Avogadro's hypothesis).
Law of diffusion.	
Abnormal incompressibility, especially at high pressures.	The molecules themselves are incompressible.
Abnormal compressibility, especially at low pressures.	The tendency to cohesion becomes evident under some circumstances.

Critical Phenomena. — We may now use the terms of the kinetic-molecular hypothesis in describing a property of gases not yet discussed. When the concentration of a gas at ordinary temperatures is greatly increased by compression, the cohesive forces have an opportunity to produce liquefaction. In many cases, as with sulphur dioxide and carbon dioxide, when the approximation of the molecules has reached a certain point, the liquid begins to form on the sides of the vessel. The condition is then exactly the same as that of aqueous vapor and water (p. 117), and no further increase in pressure is required to complete the liquefaction of the whole. The *only* difference between steam, at a pressure below the aqueous tension of water at 10°, and carbon dioxide at the same temperature, is that not more than 9.1 mm. of pressure is required to liquefy the steam, while about 50 atmospheres are needed to liquefy the carbon dioxide.

There are some gases in which, at the ordinary temperature, even with the closest approximation of the molecules, the cohesion is unable to overcome the motion of the molecules and draw the material together into the more compact liquid form. Such gases are hydrogen, oxygen, nitrogen, and air, which is a mixture of the last two. The remedy is obvious. We know of no way to increase the intrinsic cohesiveness of

the material, but we can reduce the kinetic energy of the molecules by lowering the temperature of the gas. When this has been done sufficiently, compression is followed by liquefaction. Now it is found that there is a critical value for each individual gas to or beyond which the kinetic energy must be reduced by lowering the temperature, before the cohesive tendency of that particular gas can become effective to produce liquefaction. The highest temperature below which liquefaction is possible is called the **critical temperature**. For oxygen this temperature is $-118°$, for hydrogen about $-234°$, for nitrogen $-146°$. For carbon dioxide it is 31.35°, for sulphur dioxide 156°, for water 358°. The temperature of a room being below the critical point of the last three substances, they are all liquefiable without cooling, and more easily the farther the ordinary (say 20°) lies below the critical temperature.

The foregoing is an example of how the images furnished by an hypothesis assist us in understanding facts, and how the figurative language it suggests enables us to explain the relations of the facts briefly and vividly. In interpreting statements like the above, however, we must carefully distinguish between the facts they contain, which are permanent, and the fictions and figures of speech in which we have clothed them. The wrappings will doubtless go out of fashion and change in the future, as they have done in the past, in response to our preference in emphasizing some different inter-relation in the growing body of truth. The kinetic hypothesis is already considered out of fashion in some quarters.

Kinetic Hypothesis Applied to Liquids. — The phenomena connected with surface tension, such as coherence into drops, show that cohesion plays a larger part in liquids than in gases. The formation of vapor from cold liquids, however, requires us to suppose, using the terms of the hypothesis, that motion of the molecules has not been annihilated by cohesion. To be consistent, we have also to imagine that the vapor above the liquid, for example the water in the barometer tube in Fig. 39 (p. 116), is not composed of the same set of molecules one minute as it was during the preceding minute. Their motions must cause many of them to plunge into the liquid, while others emerge and take their places. When the water is first introduced, there are no molecules of vapor in the space at all, so that emission from the water predominates. The pressure of the vapor increases as the concentration of the molecules of vapor becomes

greater, hence the mercury column falls steadily. At the same time the number of gaseous molecules plunging into the water per second must increase in proportion to the degree to which they are crowded in the vapor. Hence the rate at which vapor molecules enter the water must eventually equal that at which other molecules leave the liquid. At this point, occasion for visible change ceases and the mercury comes to rest. We are bound to think, however, of the exchange as still going on, since nothing has occurred to stop it. The condition is not one of rest but of rapid and equal exchange. Such, described in terms of the hypothesis, is the state of affairs which is characteristic of a condition of **equilibrium** (p. 117). The condition is kinetic, and not static.

To get a clear notion of a state of equilibrium, we must distinguish two *opposing* tendencies, which when equilibrium is reached balance one another. In the barometer at rest, for example, there are the two pressures, that of the air and that of the mercury. Here, one is the hail of molecules leaving the liquid which is constant throughout the above experiment. It represents the **vapor tension of the liquid** (p. 116). The other is the hail of returning molecules which increases steadily, at first, as the concentration of the vapor becomes greater. This is the **vapor pressure of the vapor**. These have the effect of opposing pressures, and when the latter becomes equal to the former, equilibrium is established. Both are still at work, but neither can effect any visible change in the system. The kinetic point of view we have here used is employed so continually in chemistry that it should be studied attentively.

When the temperature of a liquid is raised, the kinetic energy of its molecules is increased, the rate at which they leave its surface becomes greater, the vapor tension increases, and, hence, a greater concentration of vapor can be maintained. This puts into the language of our hypothesis, the change in vapor tension with temperature (p. 116).

When the liquid is placed in an *open* shallow vessel, there is practically no return of the emitted molecules. Hence complete evaporation takes place. Elevation of the temperature hastens the process. A draft insures the total prevention of all returns, and has therefore the same effect. The two methods of assisting the forward displacement of an equilibrium, and particularly the second, in which the opposed process is weakened and the forward process triumphs solely on this account, should be considered attentively (see Chap. xv).

Diffusion in Liquids.—We are further compelled, in applying our hypothesis, to suppose that there is motion of the molecules *inside* the liquid. When alcohol, as the lighter liquid, is floated upon water in a cylinder (Fig. 47), the plane separating the liquids is at first easily visible. But soon it becomes obliterated. The water diffuses upward, and the alcohol downward, each sifting its way through the other in spite of gravity. The complete mixing of the liquids takes a much longer time than in the case of two gases. It may take months. But even here the hypothesis helps us by pointing to the vast impediment which the close packing of the molecules must place in the way of the progress of any one molecule. Further, once the mixture is formed, no tendency to spontaneous separation is ever observed. Here again, the hypothesis shows that none is to be expected. If it occurred, it would be immediately undone by diffusion.

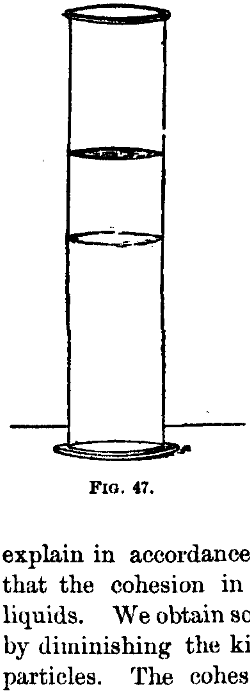


FIG. 47.

Kinetic Hypothesis Applied to Solids.—The properties of solids differ from those of liquids chiefly in the fact that the solid has a definite form of which it can be deprived only with difficulty. This we may explain in accordance with the kinetic hypothesis by the supposition that the cohesion in solids is very much more prominent than in liquids. We obtain solids from liquids by cooling them; in other words, by diminishing the kinetic energy and therefore the velocity of the particles. The cohesive tendency of the latter is thus able to make itself felt to a greater extent. If, conversely, we heat a solid, or, according to the hypothesis, if we increase the speed with which the particles move, the body first melts and gives a liquid, and this finally boils and becomes a gas. The intrinsic cohesion of the particular substance can undergo no change, but the increasing kinetic energy of the particles steadily and continuously obliterates its effects. Yet some motion still survives in a solid. Thus we find that when the layer of silver is stripped from a very old piece of electroplate the presence of this metal in the German silver or copper basis of the article is easily demonstrated.

Roberts Austen has found that if bars of lead are prepared, in one end of which an alloy containing a certain proportion of gold has been used, while the remainder of the bar is composed of pure lead, the gold has a tendency to wander slowly into the pure lead. The process is greatly aided by keeping the bars at a fairly high temperature, but one much below the melting-point is amply sufficient. After a suitable interval of time the bar may be sawn into fragments of equal length, and its parts analyzed. The quantity of gold in a section is found to increase as we approach the portion of the bar to which originally the whole of the gold was confined.

The tendency of all solids to assume crystalline forms, which show definite cleavage and other evidences of **structure**, distinguishes them sharply from liquids. The force of cohesion in liquids is exercised equally in different directions. In solids it must differ in different directions in order that structure may result. Since each substance shows an individual structure of its own, these directive forces must have special values in magnitude and direction in each substance.

A crystal arises by growth. When the process is watched, as it occurs in a melted solid or an evaporating solution, the slow and systematic addition of the material in lines and layers, as if according to a regular design, is one of the most beautiful and interesting of natural phenomena. The fern-like patterns produced by ice on a window-pane show the general appearance characteristic of crystallization in a thin layer. A larger mass in a deep vessel gives forms which are geometrically more perfect. From its very incipiency the crystal has the same form as when, later, its outlines can be distinguished by the eye. Hence the outward form is only an expression of a specific internal structure which the continual reproduction of the same outward form on a larger and larger scale leaves as a memorial of itself in the interior.

Crystal Forms.—Crystalline form is so continually used in identifying (p. 36) the substances produced in chemical actions that a list of the kinds of forms which occur will assist in giving definite meaning to our descriptions.

The classification of crystalline forms is carried out according to the degree of symmetry of the crystals. Thirty-two distinct classes are distinguished, but for our purpose a rougher division into six groups will suffice. These groups are known by the following names:

1. Regular system.
2. Quadratic, or square prismatic system.
3. Hexagonal system.
4. Rhombic system.

5. Monosymmetric, or monoclinic system.
6. Asymmetric, or triclinic system.

The **regular system** presents the most symmetrical figures of all. Some forms which commonly occur are the octahedron (Fig. 48) shown by alum, the cube (Fig. 6, p. 13) affected by common salt, and the dodecahedron (Fig. 49) frequently assumed by the garnet.

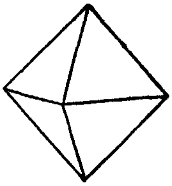


FIG. 48.

The **square prismatic system** includes less symmetrical forms than the previous one, since the crystals are lengthened in one direction. Fig. 50 shows the condition in which zircon ($ZrSiO_4$), which furnishes us with the basis of certain incandescent illuminating arrangements, occurs in nature. The form of ordinary hydrated nickel sulphate ($NiSO_4$, $6H_2O$) is similar to this.

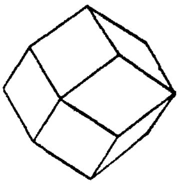


FIG 49.

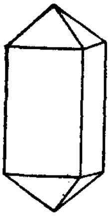


FIG. 50.

The **hexagonal system**, like the preceding, frequently exhibits elongated prismatic forms, but the section of the crystals is a hexagon instead of a square, and the termination is a six-sided pyramid. Quartz (Fig. 51), or rock crystal, is the most familiar mineral in this system. Calcite ($CaCO_3$), which is chemically identical with chalk, or marble, takes forms known as the scalenohedron (Fig. 52) and rhombohedron (Fig. 9, p. 14), which are classified in a subdivision of this system. Indeed, recently it has become common to erect this into a separate system (the trigonal), in which both quartz and calcite are included.

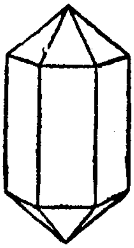


FIG. 51.

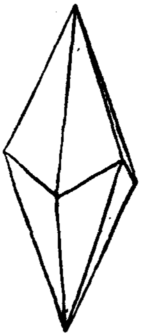


FIG. 52.

The **rhombic system** includes the natural forms of the topaz, and of sulphur (Fig. 1, p. 11), as well as that of potassium permanganate (Fig. 53), potassium nitrate (Fig. 98), and many other substances. These crystals exhibit a good deal of symmetry, but their section is always rhombic, and hence the name.

The **monosymmetric system** exhibits forms which have but one plane of symmetry. Gypsum (Fig. 54), which is hydrated calcium

sulphate ($CaSO_4$, $2H_2O$), and felspar are minerals possessing forms of this kind. Tartaric acid, rock candy (Fig. 55), potassium chlorate, and hydrated sodium carbonate (washing soda) belong to this system.

The **asymmetric system** includes forms which have no plane of symmetry whatever. Blue vitriol (Fig. 41, p. 120), ($CuSO_4$, $5H_2O$), is one of the most familiar substances of this kind.

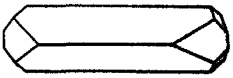


FIG. 53.

The forms of crystals which we may actually make seldom correspond exactly with the figures. If we allow a crystal to grow upon the bottom of a vessel, for example, it will usually have a tendency to spread itself out parallel to the surface of the glass, and when taken up for examination will be found to present a somewhat distorted form. By changing, at frequent intervals, the face on which the crystal stands, however, uniform growth in all directions is secured. Hanging a small crystal by a thread insures almost ideal development. Yet the form even of distorted crystals can readily be recognized by suitable means. The shape of the faces may indeed be extremely misleading. We find, however, that the angles at which the faces meet are always the same, whatever disproportionate growth may have occurred in the development of the crystal.

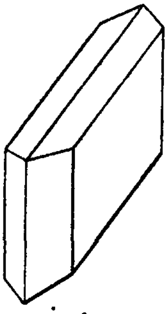


FIG. 54.

Since, in general, each substance has a form of its own, no other substance, as a rule, can be used even partially in building up the crystal (see, however, Isomorphism). This fact is taken advantage of in order to separate chemical substances from impurities. The impure body is first dissolved in some solvent. The preponderating substance in the mixture, unless it is very much more soluble than the impurity, will then usually give pure crystals while the foreign body remains in solution.

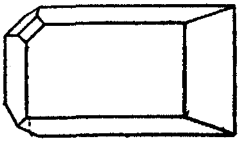


FIG. 55.

The shapes of gems must not be confused with crystalline forms. The original crystals are cut and polished to a new form specially adapted to increase the ornamental value of the stone by causing it to reflect more light (see Diamond). Again, glass is really a very viscous fluid (amorphous body, p. 123), and has no structure or form of its own.

The word "crystal" applied to cut glass would therefore be misleading if taken literally.

Crystal Structure. — As the above would lead us to expect, the study of crystallized substances shows that their peculiarities are not confined to the outside layer. The outline represents a certain structure which permeates the whole mass. In crystals of the regular system, many of the ordinary physical properties are the same as those of an amorphous substance, like glass. For example, if we turn a sphere out of crystallized salt and hang it in pure water, we find that solution takes place at a uniform rate all over the surface. This is not the case, however, with substances from any of the other systems. Spheres cut from substances belonging to the second and third systems would dissolve more, or less, rapidly in the direction of the chief axis than in any other direction, and so ellipsoids of revolution would quickly be produced. In the other three systems, more complex forms would result.

The tenacity of crystals, to whatever system they may belong, is different in different directions. Thus, a crystal of salt has a cleavage parallel to any of the faces of the cube, and, therefore, splits most easily in one of three directions at right angles to each other. Calcite, whatever the outward form of the crystal, always cleaves so as to give a rhombohedron. Fluorite (CaF_2), although almost always cubical in form, splits when broken so as to give an octahedron.

The behavior of crystals towards light is also extremely interesting. The rate at which light moves through crystals of the regular system is the same in all directions. In other crystals, however, we find that it moves with a different speed in different directions, the variations in speed being likewise related to the outward form. Finally, if a thin slab of rock salt is covered with wax and the point of a heated cone of metal is placed in the center, the wax melts uniformly in a circle around the point, indicating that the heat is conducted with equal speed in all directions. The way in which the slab has been cut with reference to the surface of the crystal, in the case of substances of the first of the above systems, has no effect upon this result. In all other cases, however, the zone of melting wax is in general elliptical, or even more complex in form, according to the system to which the substance belongs and the direction in which the slab has been cut.

Molecular Magnitudes. — Taking the properties of matter on the one hand and the assumptions of the molecular hypothesis on the other, we can estimate the degree of mutual proximity which must be assigned to the molecules in order that the hypothesis may be consistent with the facts. By considering the thickness, or rather the thinness, of thin films, certain properties of gases, and other phenomena, fairly coincident, independent values have been obtained. According to Lord Kelvin, 1 c.c. of gas at 0° and 760 mm. contains not less than 10^{20} (that is, 1 followed by twenty ciphers) molecules. A globe of water as large as a football, if magnified to the size of the earth, the component molecules being magnified at the same time, would show a

structure coarser than a heap of small shot but less coarse than a heap of footballs. The former estimate, in regard to gases, leads by calculation to the conclusion that one molecule of hydrogen weighs 0.9×10^{-24} g., or 9 over 1 followed by twenty-five ciphers of a gram. The speed of a hydrogen molecule between collisions must be about 1840 meters per second. That of an oxygen molecule must be one-quarter of this, being, according to the law of diffusion (p. 108), inversely as the square roots of the densities.

Formulative and Stochastic Hypotheses. — The nature and use of an hypothesis like the one we have been discussing will now be evident. It is a structure existing in the imagination. It cannot exist anywhere else, because it includes novelties like perfectly elastic bodies in perpetual motion. In making it, we are well aware of the inverity of some of its elements. But then, as will have been observed, we do not attempt to verify the hypothesis itself. We did not make it in order to have before us the actual structure of matter, but in order to have a sort of mechanical moving diagram which should assist us in following the behavior of matter. It is like a scaffolding, constructed to enable us to examine or work upon a difficultly accessible part of a building, which we never for a moment think of as being a part of the building. It is a sort of formula. The algebraic formula represents magnitudes; the geometrical, directions and dimensions. The formula in physics, by the use of mathematical conventions, pictures, for example, some mode of behavior of matter. For so concrete a subject, however, the mathematical mode of expression is intensely abstract. And so a representation in terms of mechanism, which is still a formula, is frequently resorted to. The molecular hypothesis is therefore a formula consisting of imaginary machinery. Its object is simply to help us in organizing or formulating knowledge on a certain subject. Hence we name it a **formulative hypothesis.**

A formula, in the very general sense in which we have used the word above, is anything which has certain properties of the nature of form in common with some other thing or relation of things. For example, the plan of a city and a blackboard diagram are formulæ. In chemistry, a "model" of some carbon compound, made up of balls of wood and wires, is just as much a formula as are the written symbols showing the constitution of the substance. It is intended to explain the behavior of the substance. From this sort of mechanical formula it is but a step to one consisting of moving particles and intended to explain the behavior of gases. The fact that this model cannot actually be constructed, because perfectly elastic materials are not available, does not alter the case one whit.

The value of the present formulative hypothesis, and of formulative hypotheses in general, is shown by the history of science. Dalton, who first worked out a clear conception of the independent behavior of mixed gases (p. 88), used this hypothesis constantly in that work. Clear understanding of the separate existence of aqueous vapor in the air could be reached by him only by thinking of each material as being made up of independent molecules. Any other mode of conceiving the mixture that might readily occur to one would involve some adhesion or interference of the two substances. His recognition of the independent solubilities of mixed gases, in proportion to the partial pressures of each, would have been delayed or prevented altogether if, in studying the results of his experiments, he had not reached it by way of this hypothesis.

Other formulative hypotheses, showing the same contradiction of plain facts in their fundamental assumptions that we have noted in the molecular hypothesis, have been and are in common use. The conception of light as consisting of corpuscles was such an hypothesis in its day. The imponderable-matter (note the contradiction) view of heat was another. The undulatory theory of light, which postulates a perfectly elastic ether, weightless, frictionless, and lacking every trace of impenetrability, is an hypothesis showing the same inverifiable elements. It is handled characteristically also, for we do not try by its means to learn more about ether, but more about light.

An essentially different kind of hypothesis is constantly used at every step in investigation, although it is seldom mentioned in books. When Mitscherlich discovered that Glauber's salt (p. 121) gave a definite pressure of water vapor, he at once formed the hypothesis, that is, supposition, that other hydrates would be found to do likewise. Experiments showed this supposition to be correct. The hypothesis was at once displaced by the fact. This sort of hypothesis predicts the probable existence of certain facts or connections of facts, hence, reviving a disused word, we call it a **stochastic hypothesis** * (Gk. στοχαστικός, apt to divine the truth by conjecture). It differs from the other kind in that it professes to be composed entirely of verifiable facts and is subjected to verification as quickly as possible. In the case of a formulative hypothesis we have no expectation, or at best a very remote one, of verifying the hypothesis, because many of its essential constituents are contrary to experience. At all events, our efforts are bent, not to verifying the hypothesis itself, but to verifying the relations between facts which it suggests.

We may **define a formulative hypothesis** as follows: A structure, the *essential parts of which are assumed facts or connections of facts more or less inconsistent with known facts, used in formulating other known facts.* It achieves this by virtue of certain logical and formal correspondences which exist

* The author owes to Professor Paul Shorey, head of the department of Greek in the University of Chicago, the suggestion of this word.

between its abstract qualities and those of the facts it is employed to explain. The verification of the assumed facts is not in question, since their inverity is one of the premises, but that of the relations between the ascertained facts which emerge, is the step to which the making of the hypothesis was only a preliminary. This sort of hypothesis, therefore, is a sort of formula, or has the properties of a formula.

A **stochastic hypothesis** is: A supposition of the existence of certain facts, or connections of facts. It is reached by deduction from other facts or connections of facts already ascertained, and is intended to be subjected to ultimate verification.

The word **theory** is applied to both kinds of hypotheses. A study of the usages of the word and of the definitions given by the best authorities does not reveal the existence of any essential qualitative difference between a theory and an hypothesis, so that a sharp distinction cannot be drawn between them. To avoid confusion, we shall use the word "theory" as a rule only in the sense in which it occurs in phrases like "the theory of heat," or "theory and practice." Here it refers to an aggregate of conceptions and largely or wholly verified generalizations and laws which constitute the abstract (as distinct from the concrete) statement of the content of some branch or phase of knowledge, so far as this has undergone successful organization.

Lest it should be imagined that the discovery of a sufficiently extensive and complete correspondence between a formulative hypothesis and the facts with which it deals constitutes, *ipso facto*, a proof of the verity of the hypothesis itself, it must be stated explicitly that such an inference is entirely illogical. Yet this fallacy is one of the commonest into which the student of science falls. This inference would be equivalent to asserting the impossibility of devising any other hypothesis which should correspond equally well with the facts. Apart from the formal illogicality of such an inference, experience has taught us that sooner or later we always encounter some feature in the behavior of the subject of the hypothesis which is different from that which the hypothesis would have led us to expect. Thus the corpuscular hypothesis to explain light, after long and useful service, had finally to be discarded (see also Atomic hypothesis).

The philosophy of the molecular hypothesis is discussed by Stallo, *Concepts and Theories of Modern Physics*, Chap. vii; Pearson, *Grammar of Science*, Chap. vii; James Ward, *Naturalism and Agnosticism*, Lectures iv and v, and many other writers.

The value of the kinetic-molecular conception as a formulative hypothesis has been illustrated in connection with critical phenomena, and will appear again when we deal with solutions and chemical equilibrium. But indeed its field of application is coextensive with the science itself.

The conceptions of the kinetic hypothesis are of especially great assistance in rationalizing chemical manipulation and so hastening the acquisition of an intelligent control of it. The constructive imagination, on the use of which experimental work depends so much for its success, must have something to work with, and this hypothesis furnishes a tool such as it requires. Methods taught by rule

of thumb are slowly learned and constantly fail in application. We may be told a dozen times that using reagents in finely powdered, or metals in granulated condition hastens all interactions, and still never think of this abstraction when working. But if it is suggested that, in terms of the kinetic hypothesis, molecules must meet freely in the same medium to react easily, and that, therefore, the larger the surface the more copious will be the supply of molecules dissolving, we are likely to form a conception of the reason for the procedure that will be lasting.

When a student is told to concentrate a solution and set it aside to crystallize, why does he evaporate the liquid rapidly to dryness, and still expect the residue to appear in large, well-formed crystals? Because he has no notion of the necessary slowness of the process. But if he has the idea that it is like building a house, one stone at a time, and that there are far more units to be laid down according to plan in making the smallest visible crystal than there are bricks in building the largest factory, his procedure may promptly become more rational.

CHAPTER X

SOLUTION

We have frequently made use of the fact that certain substances form with others homogeneous systems which we call solutions. Sometimes this property is taken advantage of for separating materials, as in the case of the removal of sulphur from admixture with iron and ferrous sulphide (p. 11). In other cases we carry out the interaction of chemical substances, by first dissolving them in some liquid and then mixing the solutions. The liquid, commonly water, is used as a vehicle for one or more of the substances, and takes no part in the chemical change. Thus some knowledge of the properties of solutions is absolutely necessary in order that we may employ them intelligently. In what follows, we shall give a preliminary account of some of the simpler facts about solution.

General Properties of Solutions. — A solid may be distributed through a liquid either by being simply suspended (p. 113) in the latter (mixture) or by being dissolved in it (solution). Similarly a liquid may be suspended in droplets in another, as in milk (emulsion), or it may be dissolved. It is usually easy to distinguish between the two cases, for a suspended substance *settles* or separates sooner or later, while a dissolved one shows *no such tendency*. The cases are exceptional where the subdivision of a suspended substance is so minute (colloidal solution) as to make its retention by filter paper impossible. If a liquid is opalescent or opaque, then we have a case of suspension. A solution is a clear, transparent, perfectly homogeneous liquid, in which the dissolved substance seems to have been dispersed so completely that the liquid cannot be distinguished by the eye from a pure substance.

There is no limit to the amount of dissipation which may thus be produced. A single fragment of potassium permanganate, for example, which gives a very deep purple solution in water, may be dissolved in a liter or even in twenty liters of water, and the purple tinge which it gives to the liquid will still be perfectly perceptible in

every part of the larger volume. The characteristics, therefore, of solution are absence of settling, homogeneity, and extremely minute subdivision of the dissolved substance.

The Scope of the Word. — The word is used for other systems than those containing a solid body dissolved in a liquid. Thus, liquids also may be dissolved in liquids, as alcohol in water. Again, if we warm ordinary water, bubbles of gas appear on the sides of the vessel before the water has approached the boiling-point. They are found to be air. Further study of the subject shows that agitation of any gas with water results in the solution of a large or small quantity of the gas, and heat will usually drive the gas out again. It appears therefore that solids, liquids, and gases can equally form solutions in liquids.

The absorption of hydrogen by palladium (at all events after a certain point) and by iron takes place in accordance with the same laws as the solution of solids in liquids, and the results may be described therefore as true solutions. Liquids are in some cases absorbed by solids, and homogeneous mixtures of solids with solids are perfectly familiar. The sapphire is a solution of a small amount of a strongly colored substance, in a large amount of colorless aluminium oxide. It may therefore be stated that solution of gases, liquids, and solids in solids appears to be possible.

Limits of Solubility. — The next question which naturally occurs to us is as to whether the mingling of two substances in this manner has any limits. We find that the results of experiment in this direction may be divided into two classes. Some pairs, of liquids particularly, may be mixed in any proportions whatever. Alcohol and water is such a pair. On the other hand, at the ordinary laboratory temperature, we can scarcely take a fragment of marble ($CaCO_3$) so small that it will dissolve completely in 100 c.c. of pure water. Under the same conditions any amount of potassium chlorate up to 5 g. will almost completely disappear after vigorous stirring, while 90 g. of ordinary Epsom salts (hydrated magnesium sulphate), but not more, may be dissolved in about the same amount of water. In fact, most solids may be dissolved in a liquid only up to a certain limit, which with different solids may range from a scarcely perceptible to a very large amount. No substance is absolutely insoluble. But for the sake of brevity we call marble, for example, "insoluble" because in most connections it may be so considered.

Recognition and Measurement of Solubility. — The only method of recognizing with certainty whether a solid is soluble in a liquid or not is to filter the mixture and evaporate a few drops of the filtrate on a clean watch-glass. For learning how much of the body is contained in a given solution, a weighed quantity of the solution is evaporated to dryness and the weight of the residue determined. When the dissolved substance is volatile, its presence is often shown by some chemical test (p. 99).

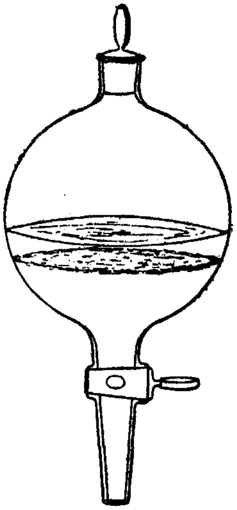


FIG. 56.

Ether and water is a case typical of the behavior of two liquids, each somewhat soluble in the other. After being shaken together, they seem to separate again completely into two layers (Fig. 56) with the ether uppermost. If, however, the water is withdrawn from beneath the ether, we find that, when heated, it gives off quantities of ether vapor which can be set on fire. Conversely, the addition of anhydrous cupric sulphate to a sample of the ether shows the presence of water in the latter, for the blue hydrated form of the substance is at once produced. In some common cases the maximum solubilities at 22° are as follows:

SUBSTANCE.	GRAMS OF SUBSTANCE IN 100 GRAMS OF WATER.	GRAMS OF WATER IN 100 GRAMS SUBSTANCE.
Alcohol	No limit	No limit
Ether	2.16	11.02
Chloroform	0.64	0.10
Carbon disulphide	1.24	0.13

It must be stated explicitly that in going into *solution*, as we have used the term, a compound dissolves as a whole, and, if the compound is pure (p. 34), any residue has the same chemical composition as the part which has dissolved.

Terminology. — In order to describe the relations of the components of a solution, certain conceptions and corresponding technical expressions are required. It is customary to speak of the substance

which, like water in most cases, forms the bulk of the solution, as the **solvent**. To express the substance which is dissolved, the word **solute** is frequently used, and will be employed when we wish to avoid circumlocution. The term "strength" is too indefinite for scientific purposes. It may imply activity, or power of resistance, or pungency (in an odor), or, as in the case of solutions, it may be a measure of quantity. The amount of the substance which has been dissolved by a given quantity of the solvent is therefore described as the **concentration** of the solution. A solution containing a small proportion of the dissolved body is called **dilute**; it has a small concentration. One which contains a larger amount is **more concentrated**. Very "strong" solutions are frequently spoken of simply as **concentrated solutions**. The *partial* removal of the solvent by evaporation is called **concentrating**, its total removal **evaporating to dryness**. Finally, since there is a limit to the solubility of most substances, a solution is described as **saturated** when the solute has given as much material to the solvent as it can. This state is reached after prolonged agitation with *an excess* of the gas, the liquid, or the *finely powdered* solid, as the case may be. The larger the excess, the sooner saturation is attained. The maximum concentration attainable in this way is called the **solubility** of the substance in a given solvent.

The distinction between solute and solvent is made merely for convenience. Theoretically there is no distinction between the components of a solution.

The concentrations of solutions, saturated and otherwise, are sometimes expressed in physical, and sometimes in chemical, units of weight. When physical units are employed, as in the above table, we give the number of grams of the solute held in solution by one hundred of the solvent, or, occasionally, the number of grams in one hundred of the solution.

When chemical units of weight are employed, two different plans are possible, and both are in use. Either the equivalent (p. 49) or the atomic weights may be taken as a basis of measurement. In the former case, the solutions are called **normal solutions**, and in the latter, for a reason which will appear later (Chap. xii), **molar solutions**.

A normal solution contains one gram-equivalent of the solute in one liter of solution. The word "equivalent" has been used hitherto only of elements, and this application of the expression involves an extension of its meaning. **An equivalent weight of a compound is that amount of it which will interact with one equivalent of an element.** Thus, a

formula-weight of hydrochloric acid HCl (36.5 g.) is also an equivalent weight, for it contains 1 g. of hydrogen, and this amount of hydrogen is displaceable by one equivalent weight of a metal. A formula-weight of sulphuric acid H_2SO_4 (98 g.), however, contains two equivalents of the compound, and a formula-weight of aluminium chloride $AlCl_3$ (133.5 g.) three equivalents. Hence normal solutions of these three substances contain respectively 36.5 g. (HCl), 49 g. (H_2SO_4), and 44.5 g. ($AlCl_3$) per liter of solution. The special property of normal solutions is, obviously, that equal volumes of two of them contain the exact proportions of the solutes which are required for complete interaction. Solutions of this kind are much used in quantitative analysis.

Solutions of different concentrations all prepared on the above basis are named as follows, and are often indicated by the abbreviations appended:

QUANTITY OF SOLUTE PER LITER.	NAME.	ABBREVIATION.
One hundredth of one gram-equivalent	Centi-normal	$\frac{N}{100}$ or .01 N
One tenth of one gram-equivalent	Deci-normal	$\frac{N}{10}$ or .1 N
One half of one gram-equivalent	Semi-normal	$\frac{N}{2}$ or .5 N
One gram-equivalent . . .	Normal	N
Two and a half gram-equivalents	Two and a half normal	$2\frac{1}{2}$ N or 2.5 N

A molar solution contains one mole (gram-molecular weight) of the solute in one liter of solution. When molecular formulæ (see Chap. xii) are used, this means one gram-formula weight per liter. In the cases cited above, the molar solution contains 36.5 g. (HCl), 98 g. (H_2SO_4), and 133.5 g. ($AlCl_3$) per liter. As will be seen, the concentration of molar and normal solutions are necessarily identical when the radicals are univalent. Other concentrations are described as deci-molar ($M/10$ or .1 M), two and a half molar (2.5 M), and so forth, on the same plan as before.

There is also a chemical unit of **volume** (see Chap. xii) which is the volume occupied by a mole (gram-molecular weight) of a gas (or dissolved substance) at 0° and 760 mm. pressure (gaseous or osmotic). This volume averages 22.4 liters, and is called the gram-molecular or **molar volume** (G. M. V.). The unit of concentration for many theoretical purposes is, therefore, that of one mole in 22.4 liters.

Solution One of the Physical States of Aggregation of Matter. — When a solid body dissolves in a liquid, the properties of the body undergo a very marked change, which to all appearance might be

chemical. Yet, besides the ease with which a liquid may be removed by evaporation and the solid recovered unchanged, we note particularly that the concentration of a saturated solution cannot be expressed in terms of integral multiples of the chemical combining weights. If, therefore, the process were to be regarded as chemical, several important generalizations would have to be revised or discarded (*cf.* p. 48). We shall see also, in a later paragraph, that the quantity of a solid which a liquid may take up varies with the slightest change in temperature. Now we do not find the composition of chemical compounds so to vary. The solution of a solid may therefore be likened to a change in state, such as the conversion of a liquid into a gas or a solid.

As there is danger of confusion arising, we may repeat that a compound is homogeneous and its composition is expressible in chemical units of weight; a saturated solution is homogeneous but its concentration varies with temperature so that chemical units cannot be used to describe its composition; a mixture, as of two solids or two liquids, is neither homogeneous nor in any way definite in composition.

Kinetic-Molecular Hypothesis Applied to the State of Solution. — Accepting solution as a physical state, we may now apply the same formulative hypothesis to the explanation of the behavior of a substance in solution as to matter in the gaseous or liquid states. We saw that a solid body, which is ordinarily condensed in a small space, can be disseminated by the use of a solvent through a very large one. The molecules of the solid become scattered like those of a gas or vapor through a much greater volume. We may regard the dissolved substance as being, practically, in a gaseous or *quasi*-gaseous condition. The molecules are torn apart from one another, their cohesion is overcome, and their freedom of motion is in a measure restored. It is true that they could not continue to occupy this large volume for a moment in the absence of the solvent. But we may bring this into relation with the case of a vapor by saying that a solid body, like common salt, can only evaporate appreciably at the ordinary temperature, and occupy a large space, when that space is already filled with a suitable liquid. The latter acts as a vehicle for the particles of the solid. A volatile liquid, on the contrary, can dissolve in an *empty* space and fill it with its particles without any vehicle being required.

This conception of the *quasi*-gaseous condition of a dissolved substance would be simply fantastic if it did not lead us to a better understanding of the behavior of solutions. Now there are certain proper-

ties of gases already discussed which we should naturally proceed to look for in the case of dissolved bodies if this theory were correct. These are the properties described under the law of diffusion, Boyle's law, and Charles' law.

It is easy to show that, if we place a quantity of the pure solvent (Fig. 57) above a concentrated solution of a substance, and then set the arrangement aside, the dissolved body slowly makes its way through the liquid (Fig. 58), obliterating the original plane of separation. Eventually the dissolved body scatters itself uniformly through the whole. In other words, the particles of the dissolved substance exhibit the property of diffusion in the same way as do those of gases.

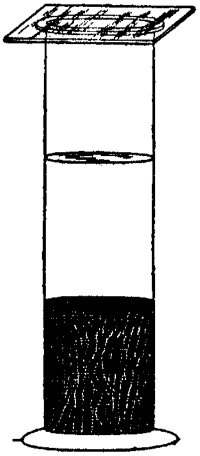


FIG. 57.

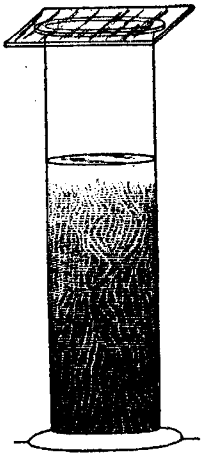


FIG. 58.

When the diffusion of a *gas* is resisted by a suitable partition, we find pressure is exercised upon the walls of the vessel and upon the partition. It is possible to show that the particles of a *dissolved substance* exercise a pressure of a very similar kind. This pressure is spoken of as **osmotic pressure** (*q.v.*). In order to get evidence of this pressure, we must place a partition between the solution and the pure solvent (Fig. 57), and we must choose the material of this partition so that its substance gives free passage to the solvent while it resists the exit of the dissolved material. The particles of the latter, then, by their impacts upon it, produce the effect of pressure exactly as in the case of gases. This pressure is found to be proportional to the concentration of the solution. In other words, it depends upon the degree of crowding of the molecules of the dissolved substance. It corresponds therefore exactly to the pressure of gases in this respect, and Boyle's law (p. 81) expresses the relation equally for both.

It may be added, also, that osmotic pressure increases when a solution is warmed, and it gains $\frac{1}{273}$ of the value it had at 0° for every degree through which the temperature is raised. In other words,

Charles' law (p. 87) describes the change in osmotic pressure with change in temperature just as correctly as it does the change in gaseous pressure.

Kinetic-Molecular Hypothesis Applied to the Process of Solution. — We may now apply the same hypothesis to the process of dissolving, with a view more especially to explaining why the process of dissolving ceases, in spite of the presence of excess of the solute, when a certain concentration has been reached. If some of the material dissolves, why not more?

Let us suppose that it is the dissolving of common salt in water (Fig. 59) which we wish to explain in detail. We believe that in the solid substance the molecules are somewhat closely packed together, while in the solution they are rather sparsely distributed. If there were no water over the salt, practically none of the particles of the latter would be able to leave the solid and enter the space above. Thus, the process of solution must consist in the loosening of the molecules on the surface and their passage into the liquid. By diffusion, the free molecules will gradually move away from the neighborhood of the surface of the solid and make room for others, and thus, if the system remains undisturbed, the liquid will eventually become a solution of uniform concentration. If a large enough amount of the solid has been provided, the ultimate condition will be that of a saturated solution with excess of the solid beneath. If we had proper means of measuring it, the tendency of the molecules to leave the solid in the presence of a given liquid would give the effect of a kind of pressure. This is spoken of as **solution pressure**.

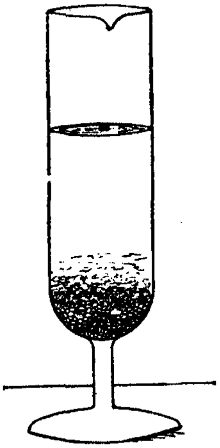


FIG. 59.

Now the molecules, after having entered the liquid, move in every direction, and consequently some of them will return to the solid and attach themselves to it. The frequency with which this will occur will be greater as the crowding of particles in the liquid increases, so that a stage will eventually be reached at which the number of molecules leaving the solid will be no greater than that landing upon it in a given time. If the whole of the liquid has mean-

while become equally charged with dissolved molecules, there will be no chance that the field of liquid immediately round the solid will lose them by diffusion, so that a condition of balance or equilibrium will have been established: NaCl (solid) $\rightleftarrows$ NaCl (diss'd). The motion of the particles in the liquid produces what we have called osmotic pressure; and when the osmotic pressure, by the continual increase in the number of dissolved molecules, becomes equal to the solution pressure, increase in concentration of the solution ceases. It is at this point that we speak of the solution as being saturated with respect to the particular substance dissolving. The analogy to vapor tension and vapor pressure (p. 135) is evident.

The necessity of distinguishing between the fictions used in thinking about and describing the phenomena of solution and the facts themselves must be emphasized here as it was in the preceding chapter. The arrangement and expression of the facts about solutions in terms of the kinetic-molecular hypothesis is known as the *theory of solutions.*

Independent Solubility. — Just as two gases, when mixed, are independent of one another (p. 88), and have severally the same pressure, solubility, and so forth, as they would possess if each alone occupied the same space, so is it with dissolved substances. In general, a volume of water, in which a moderate amount of some substance has been dissolved, will take up as much of a second substance as would an equal volume of pure water. Thus, water containing some sugar will dissolve as much sodium chloride as the same amount of pure water. In the point of view of the kinetic-molecular hypothesis, the dissolved molecules of sugar have no connection with, or influence upon, the mechanism which determines the solubility of the salt, namely, the exchange of salt molecules between the suspended, dissolving crystals and the solution.

Naturally this principle of independent solubility does not hold with any degree of exactness when the concentration of the substance already present is great. It fails also when the two solutes interact chemically, as will usually be the case, for example, when each is an acid, base, or salt (see Chap. xvi). The solubility is affected in an especial degree when the two substances have one radical in common, as when they are nitric acid and a nitrate, or two chlorides (see Ionic equilibrium).

Solution of a Gas in a Liquid. — The same conceptions may be used to explain any case of solution. Let us take that of oxygen con-

ducted into a bottle which is partially filled with water (Fig. 60), no other gas being present in the space above the liquid. As the molecules of the gas impinge upon the liquid, some of them pass into it and dissolve. The particles which have thus gained access to the liquid move about in every direction, and, as they become more and more numerous, a larger and larger number will escape from the surface and pass back into the gaseous condition. At first, this reaction will be slight, but eventually, as the solution increases in concentration, it must become equal in rate to the process of solution itself. It is assumed that the supply of gas is maintained at a uniform pressure, and therefore uniform molecular concentration, during the whole process. Once more we shall have a state of balance or equilibrium, and the liquid will be *saturated*, this time with a gas : O (gas) $\rightleftarrows$ O (diss'd). It is found, as the hypothesis would lead us to expect, that **the concentration of the saturated solution of a gas is proportional to the pressure at which the gas is supplied.** This is usually known as **Henry's law.**

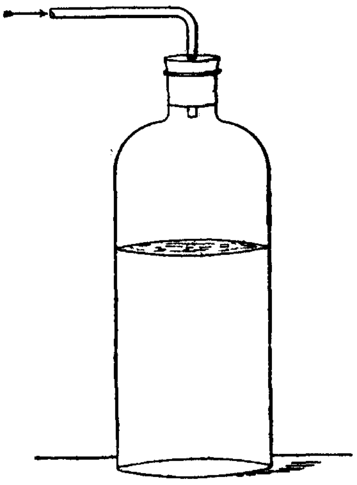


FIG. 60.

Henry's law is anticipated from the theory when we consider that the pressure of the gas is proportional to the degree of crowding of its molecules. On the other hand, the concentration that can be maintained in the saturated solution is proportional to the frequency of the impacts of the molecules of the gas upon the surface of the liquid, and this in turn will be proportional to the degree to which they are crowded in the space above the liquid. Hence the concentration of the saturated solution is proportional to the gaseous pressure.

The solubility of different gases varies much. One volume of water will dissolve 1050 volumes of ammonia at 0° and 760 mm., while it will dissolve only about 0.02 volumes of hydrogen under the same conditions. In one volume of alcohol, at 0° and 760 mm., 17.9 volumes of hydrogen sulphide or 0.07 volumes of hydrogen may be dissolved. The law describes the behavior of the bodies with exact-

ness only when low gaseous pressures and gases whose solubility is small are in question. Great solubility must be due in part, probably, to chemical union between the material of the gas and the solvent, or to cohesive influences which the molecules of the dissolved gas exert upon each other. The hypothesis, on the other hand, considers only an ideal behavior involving complete chemical and physical independence of the molecules.

When more than one gas is in contact with the solvent, the hypothesis enables us successfully to foretell what will happen. The quantity of each gas which can remain dissolved must depend simply upon the frequency with which *its own* molecules strike the liquid, and must be independent of the presence of the other gas. Hence the solubility of each gas is the same as if it were present alone at its own partial pressure (p. 88). Dalton used these very considerations in drawing this conclusion from his experimental data.

Air dissolving in water is an illustration of this principle. It does not dissolve as a whole, but the oxygen and nitrogen dissolve each in proportion to its intrinsic solubility and partial pressure.

It is easy, by the use of this law, to form an approximate estimate of the proportion of oxygen to nitrogen in the dissolved gases. The air may be taken to be at 760 mm., and its composition by volume roughly 1/5 oxygen and 4/5 nitrogen. The separate solubilities of the gases at 760 mm. are, respectively, 4 and 2 volumes in 100 volumes of water. Their partial pressures being 1/5 and 4/5 of an atmosphere, the amounts actually dissolved will be $4 \times 1/5 = 0.8$ and $2 \times 4/5 = 1.6$ in 100 volumes of water. The ratio of free oxygen to nitrogen in the water will therefore be 1 : 2.

Two Immiscible Solvents: Law of Partition. — An interesting application of the same ideas may be made to a case which occurs very commonly in chemical work. If we shake up a small particle of iodine with water, we find that it dissolves slowly, giving eventually a saturated but very dilute solution. If now ether in sufficient quantity be shaken with the aqueous solution, the greater part of the iodine will find its way into the ether, and be contained in the brown layer which rises to the top. The process of removing a substance partially from solution in one solvent and securing it in another is called **extraction**. We find in such cases that neither solvent can entirely deprive the other of the whole of the dissolved substance, if the latter is soluble in both independently: I (in Aq.) $\rightleftarrows$ I (in ether). The partition of the substance takes place in proportion to its solubility in each solvent. It is found that any amount of the solute, up to the maxi-

mum the system can contain, provided this does not involve too high a concentration in either solvent, is divided so that the ratio of the concentrations in the two solvents is always the same. In the case of iodine divided between water and ether, this ratio is about 1 : 200.

The aqueous solution of potassium iodide has a very great power of dissolving iodine, and we find that in the presence of this salt the ether leaves a much larger share of the element in the lower layer. A part of the iodine combines to form KI_3, however, so that this is not a case of simple solution, and the law of partition does not hold. The chemical equilibrium (see Chap. xv) between free and combined iodine in the aqueous layer has to be considered.

Influence of Temperature on Solubility. — The quantity of a substance which we can dissolve in a fixed amount of a given solvent depends very largely upon the temperature of both. Usually the solubility increases with rise in temperature. Measurements may be made by the method described before (p. 147), using excess of the finely powdered solute with different portions of the same solvent in vessels kept at different temperatures. The most useful way of representing the results is to plot them graphically. The diagram (Fig. 61) shows the curves for a few familiar substances. The ordinates represent the number of grams of the anhydrous compound which is held in solution by 100 g. of water in each case. The abscissæ represent the temperatures. The concentration for any temperature can be read off at once. Thus 100 g. of water holds 13 g. of potassium nitrate in solution at 0° and 200 g. at 87°. The increase in solubility is here enormous. On the other hand, the same quantity of water will hold 35.6 g. of sodium chloride in solution at 0° and 40 g. at 100°. The difference is shown at once when we examine the curves and observe that the line representing the solubility of sodium chloride scarcely rises at all between 0° and 100°, while that of potassium nitrate is extremely steep.

Cases in which the solubility decreases with rise in temperature are less common. When cold water is saturated with calcium citrate, and the solution is then warmed, a large part of the salt is quickly precipitated.

When triethylamine, an organic base, $N(C_2H_5)_3$, liquid at ordinary temperatures, is added to cold water until no more will dissolve, the solution, which is perfectly clear and transparent, on being warmed with the hand at once becomes clouded from the separation of the two liquids. A comparatively slight elevation in temperature causes a separation into two distinct layers.

Phases. — We can frequently abbreviate our statements by using two words of broad significance, one of which has already been em-

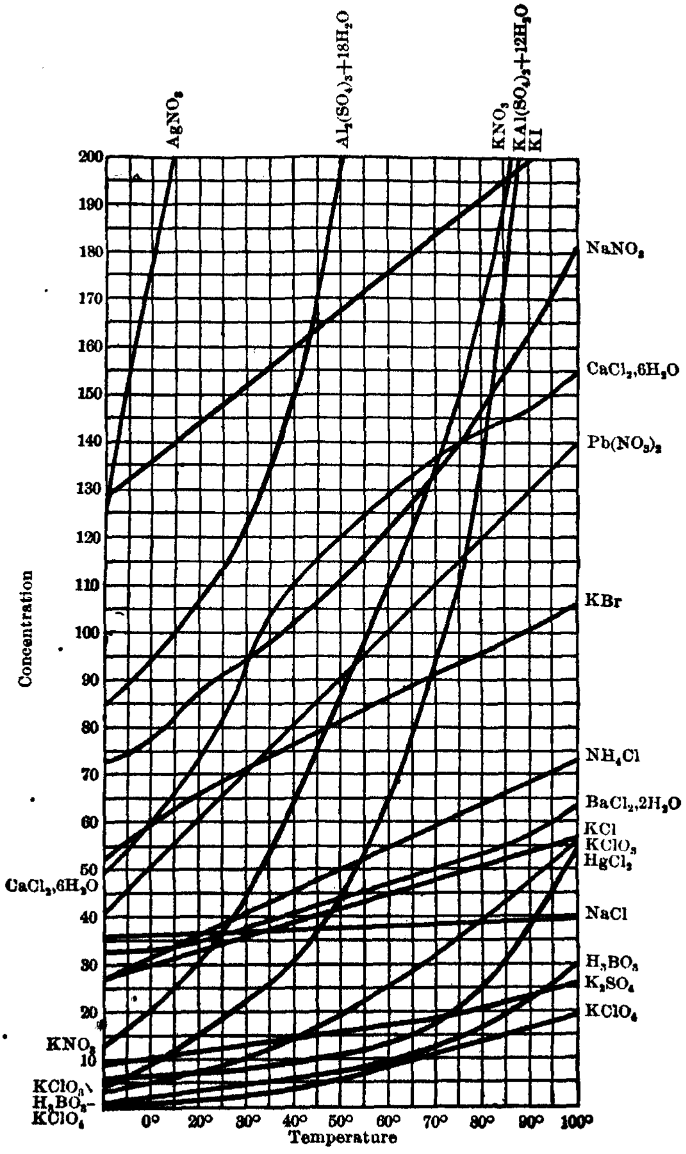

AgNO$_3$
Al$_2$(SO$_4$)$_3$+18H$_2$O
KNO$_3$
KAl(SO$_4$)$_2$+12H$_2$O
KI
NaNO$_3$
CaCl$_2$,6H$_2$O
Pb(NO$_3$)$_2$
KBr
NH$_4$Cl
BaCl$_2$,2H$_2$O
KCl
KClO$_3$
HgCl$_2$
NaCl
H$_3$BO$_3$
K$_2$SO$_4$
KClO$_4$
Concentration
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
CaCl$_2$,6H$_2$O
40
30
20
KNO$_3$
10
KClO$_3$
H$_3$BO$_3$
KClO$_4$
0°
20°
30°
40°
50°
60°
70°
80°
90°
100°
Temperature

FIG. 61.

ployed. A set of materials in or tending towards a condition of equilibrium is called a **system**. The discrete parts of an inhomogeneous system are called its **phases**. Thus, a liquid with its vapor forms a system with a liquid phase and a vapor phase. A saturated solution is a system with three phases, the undissolved excess of the solute (solid phase), the solution, and the vapor.

Equilibrium in a Saturated Solution. — Once a solution has become saturated, the dissolving substance remains thereafter unchanged in amount no matter how long the materials are left in contact. In technical terms, the quantity of each phase has no influence on the concentration of any of them. A greater excess of the solute forces no more matter into solution than does a small excess.

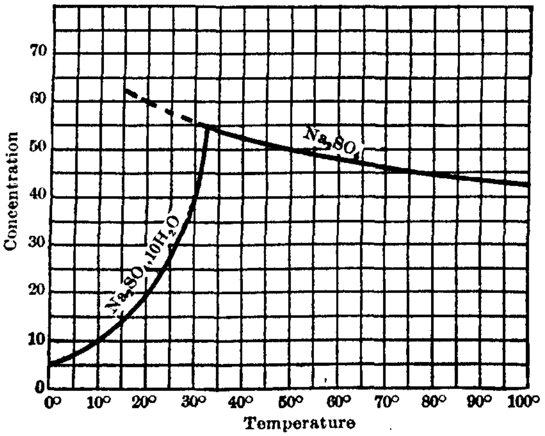


FIG. 62.

It should be clearly understood that the kinetic hypothesis requires us to assume that an exchange of molecules (p. 135) is still going on between the solid and the solution. That this conception is correct may be shown in various ways. Thus, if a crystal, the edges or corners of which have been broken, is suspended in a saturated solution of the same substance, it neither increases nor diminishes in weight Yet we find that the imperfections are removed, and that this takes place by the solution of a portion of the substance from the perfect surfaces and its deposition upon the imperfect ones.

Another very striking proof of this may be obtained by saturating water with ordinary Glauber's salt (hydrated sodium sulphate, Na_2SO_4, $10H_2O$) at a temperature somewhat above the ordinary, say 30°. The excess of the solid is carefully and completely separated from the liquid, and the latter is allowed to cool in a flask loosely stoppered with cotton. The solution now contains (Fig. 62) a much larger amount of

sodium sulphate (Na_2SO_4) than at its present temperature it could acquire from contact with Glauber's salt. Yet in the absence of a crystal, with which the above described exchange could take place, no deposition of the dissolved substance begins. The solution may be kept indefinitely without alteration. The introduction, however, of the minutest fragment of the decahydrate at once starts the exchange, and this is necessarily very much to the disadvantage of the solution and the advantage of the crystal: Na_2SO_4 (diss'd) $\rightleftarrows$ $Na_2SO_4, 10H_2O$ (solid). The latter therefore forms the center of a radiating mass of blade-like processes, which sprout with astonishing rapidity through the liquid.

Usually the cooling of a concentrated solution leads to the almost immediate appearance of crystals spontaneously, and the substance is deposited gradually as the temperature falls. But solutions of a number of common substances, such as sodium thiosulphate (photographer's "hypo") and sodium chlorate, behave like that of sodium sulphate. They are said to have a tendency to give **supersaturated solutions.** In general, crystallization can be started only by introduction of a specimen of the same substance, or at all events of one isomorphous (*q.v.*) with it. The smallest particle of the right material floating in the air, if it gains accidental admission, will bring about the result. This shows the importance of the interchange of molecules of which we have spoken for establishing equilibrium.

Metastable Condition. — The above phenomenon is not an isolated or exceptional one in physical science. It is commonly the case that, when the conditions for some physical change have been reached, the beginning of the physical change is delayed or entirely fails. The system is then said to be in a **metastable** condition. Unstable it is not. Yet it is not in the state of greatest stability, for the element of equilibrium is lacking. Thus, pure water may easily be cooled three or four degrees below 0° without the appearance of any ice. Agitation, however, in this case, results in the appearance of ice sooner or later. In like manner water may be heated to a temperature above 100° without boiling. Drops of water, suspended in some oil of almost the same specific gravity, may even be raised to 175° before the water turns into steam. Similarly, air which is saturated with moisture, if it contains no dust, may be cooled without the appearance of fog.

Phenomena of supersaturation, of a temporary kind at least, are extremely common in chemistry. Almost every delayed precipitation is a case of it. Barium

sulphate, for example, is always slow in appearing in dilute solutions. So is sulphur, set free from dilute sodium thiosulphate solution by the action of an acid. In the latter case, instant reneutralization with a base does not prevent the ultimate appearance of the sulphur, showing that the cause does not lie in slow interaction of the salt with the acid.

Saturation. — When we have shaken a solid for a sufficient length of time with a given amount of a liquid, we obtain a solution which is saturated with respect to that substance. Having called this a saturated *solution*, we are inclined to extract from the term a meaning different from that which it was really intended to convey. We are in danger of thinking that the solution itself is in some way peculiar — that, for instance, it contains all of the solid which it is capable of holding. This would be an entire misconception. If we desire to make a solution of sodium sulphate (Na_2SO_4), for example, we may present this substance to the water either in the form of Glauber's salt ($Na_2SO_4, 10H_2O$) or of anhydrous sodium sulphate. Now the anhydrous and the hydrated forms of a substance always behave like entirely different substances. This hydrate cannot give more than 5 parts of sodium sulphate (Na_2SO_4) to 100 parts of water at 0°. When the anhydrous compound is used, many times this amount (Fig. 62) is dissolved at the same temperature: Na_2SO_4 (solid) $\rightleftarrows$ Na_2SO_4 (diss'd). The solution pressures of the two forms are entirely different. The phrase, "a saturated solution of sodium sulphate," is therefore devoid of definite meaning. We must describe the liquid as a solution saturated by anhydrous, or by hydrated sodium sulphate as the case may be.

Being different substances, the hydrated and anhydrous forms of a compound must be investigated separately as to their solubility at various temperatures. The results must give different curves, as for distinct substances.

Before referring to the curves of the two sodium sulphates, it must be remarked that hydrates decompose into the anhydrous, or some less hydrated form at a definite temperature. We cannot therefore continue the observation of the solubility of the substance beyond the temperature at which it ceases to exist. Thus the solubility curve of a hydrate comes to an abrupt termination at the decomposition, or, as it is usually called, the *transition point*. Now the decahydrate of sodium sulphate decomposes at 32.4°, so that its solubilities can be measured only from about 0° to 32.4°. The solubility of the anhydrous form, however, can be investigated up to 100°, or beyond it, if necessary. Not only so, but measurements can be carried out below 32.4°. The union with water to form the decahydrate is so slow that there is time to saturate the solution with the anhydrous body, and decant the liquid for analysis, before the hydrate begins to be produced.

The solubility of the decahydrate (Fig. 62) rises rapidly between 0° and 32.4° from 5 to 55 parts in 100. The solubility of the anhydrous sodium sulphate de-

creases steadily from more than 55 parts below 32.4° to 42.5 parts at 100°. The character of the two bodies, in the matter of solubility, is therefore entirely different. The solutions themselves, as has been said already, are identical in every way, when they have the same concentration, whether they have been made from the one substance or the other.

Let us return now to the proper use of the term "saturated solution." We might say, correctly, that at 20° a solution made from hydrated sodium sulphate and containing 19.4 parts of sodium sulphate in 100 of water was saturated. This would *not*, however, be the maximum quantity which the same amount of water could hold, for, with the help of the anhydrous compound, we could add an amount equivalent to prolonging the ordinate at 20° until it intersected the curve of anhydrous sodium sulphate somewhere about the value 60. Nor can we be sure that even then the water would contain all the sodium sulphate which it *could hold*. It is conceivable that, by presenting the substance in some still other form, even greater solubility might be observed.

A saturated solution, if we fix our minds upon it simply as a solution, is not different from any other solution. There is no feature in the properties of such a solution *qua* solution which distinguishes it in the least from one containing slightly less or one containing slightly more of the dissolved substance. In contact with a crystal of the substance used to produce the saturation, however, the saturated solution is found to be in equilibrium, while the unsaturated solution takes up more of the substance, and the supersaturated solution at once deposits the amount which it contains in excess of the saturated solution. The words unsaturated, saturated, and supersaturated convey, therefore, no meaning unless we add that the solution is so towards some specific form of material. These are qualities of the system including the undissolved body and not of the solution by itself.

The fact that the hydrated and anhydrous sodium sulphates give saturated solutions of the same concentration at 32.4°, so that the curves intersect at this point, is a very significant one. This is the temperature at which the former substance turns into the latter. At transition points like this the values of solubility, vapor pressure, and some other properties, are always the same for both forms (see Freezing-points of solutions).

Properties of Solutions Proportional to Concentration: Vapor Tension. — Besides osmotic pressure (p. 151), there are several properties of solutions which are proportional to the concentration of the solution.

If, instead of water, we introduce aqueous solutions of the same substance successively into the barometric vacuum (Fig. 39, p. 116), we find that the **vapor pressures** of the solutions are less than that of water at the same temperature. The diminution in the fall of the mercury column, which measures **the lowering in vapor pressure, is proportional to the concentration of each solution**. The limit is reached with the saturated solution, although, if this is rather concentrated, the proportionality does not hold strictly down to that point (see Chap. xvii).

This lowering in the vapor pressure of water is often considerable. Thus at 100° a 7.5 per cent solution of potassium chloride shows a vapor pressure of only 734.1 mm., while that of water is 760 mm. The difference is 25.9 mm. Hence the solution has to be raised to a **higher temperature** (100.96°) before it boils. This is almost exactly .037° per 1 mm., which is the value for pure water (p. 118).

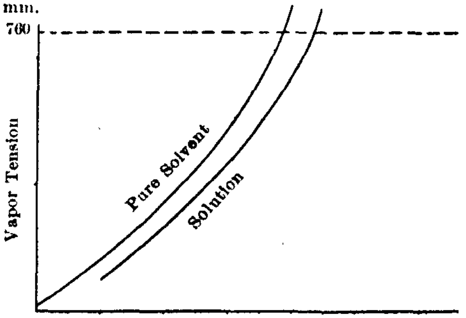


Fig. 63.

This conclusion may also be reached graphically (Fig. 63). The ordinates represent the vapor tensions corresponding to the temperatures shown by the abscissæ. They increase in length with rise in temperature. The horizontal dotted line shows the vapor tension of 760 mm. at which any liquid will boil. The boiling-point of the solvent is therefore the temperature at which its curve intersects this line. Since the vapor tensions of the solution are all below those of the solvent, its curve lies below that for the solvent but ascends along with the latter. Hence it also cuts the 760 mm. line, but at a point *beyond* the boiling-point of the pure solvent. Since, for short lengths, the curves are very nearly straight lines, the distances from boiling-point to boiling-point are very nearly proportional to the vertical distances between the curves. That is to say, the **elevations in the boiling-point are proportional** to the depressions in the vapor tension, and therefore **to the concentration of the different solutions of any one substance.** When different substances or solvents are compared, the scale alone is different (see Chap. xvii).

The same effect may be observed in isomorphous mixtures of solid bodies, which in many ways resemble solutions. Thus the vapor tension of water in the alums is greater than the average vapor pressure of water in the air, and hence they lose their water of hydration spontaneously (*cf.* p. 121). But if mixed crystals of two alums, say ordinary alum and iron alum (K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$ and $(NH_4)_2SO_4$, $Fe_2(SO_4)_3$, $24H_2O$), are prepared, they keep perfectly. The vapor tension of the water in each has been lowered by the influence of the other alum dissolved in it. Similarly, calcium formate ($Ca(CHO_2)_2$, $4H_2O$) effloresces (p. 123), but loses this tendency when crystallized with some of the isomorphous barium or strontium salt.

This principle explains the habit of very soluble compounds (**deliquescent** substances) to become moist when exposed to the air and finally to dissolve in the water they seem to attract from it. Since, on account of their solubility, the moisture first present on

their surfaces (p. 117) is a highly concentrated solution, its vapor tension is lower than the vapor pressure of water in ordinary air (p. 161). Hence further condensation takes place (pp. 121–122) until the substance is so diluted that the vapor tension of its solution becomes equal to the aqueous pressure of the atmosphere. Concentrated sulphuric acid, calcium chloride, and magnesium chloride (p. 34) are substances of this kind.

Freezing-Points of Solutions. — Every pure liquid has a definite temperature at which it freezes. Thus, pure water freezes at 0° and benzene at 6°. The presence of a foreign, dissolved body, however, lowers the freezing-point. Thus, sea-water is harder to freeze than fresh water. **The freezing-points of solutions of the same substance are found to be depressed below that of the solvent in proportion to the concentration of the solute*** (see Chap. xvii). This may be shown graphically (Fig. 64). The ordinates represent vapor tensions corresponding to the temperatures shown by the abscissæ. The rate at which the former rise is greater for ice than for water, hence the ice curve is steeper. At 0°, ice and water can coexist permanently (p. 115). By measurement, they have the same vapor tension (4.6 mm.) at this point. Theoretically, if they had not, they could not coexist indefinitely, for the one with the greater vapor tension would evaporate, and its vapor would condense on the other until one of them alone remained.

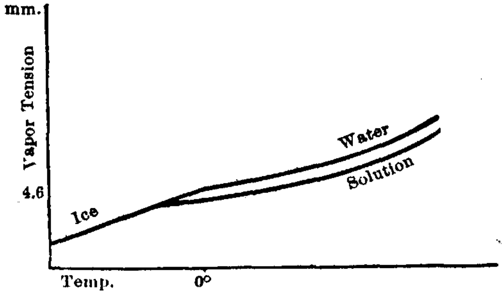


FIG. 64.

Now the vapor tension of a solution is, at all temperatures, lower (Fig. 64) than that of water. Hence, for a solution, the curve must cut the ice curve below 4.6 mm. and therefore behind 0°. In other words, ice and the solution cannot have equal vapor tensions, and therefore coexist indefinitely, except at some temperature below 0°.

* The ice which separates during the freezing consists, as a rule, of the pure solvent, and the solute does not enter into it. Only when this is the case does this law represent the facts.

But the temperature at which ice can exist indefinitely in a solution is the freezing-point. Hence, freezing-points of solutions are always lower than those of the pure solvents.

By measuring the vapor tensions of the solution at several temperatures, in order to see how far the curve for the solution is below that of water, and then producing the curve for the solution backwards, the intersection with the ice curve, and therefore the freezing-point, may be obtained graphically. Direct measurement always confirms the result.

At transition points like that of ice and water, the values of properties of both forms, such as the vapor pressure and the solubility in some different substance, are always identical.

Since the ice curve is, for a short distance, almost a straight line, it follows that the depressions of the freezing-point are proportional to those of the vapor tension, and these in turn are proportional to the concentrations. From this relation we get the statement with which this section opened. Thus, solutions of sugar containing 11.4, 22.8, and 34.2. g. of sugar to 100 g. of water freeze at $-0.62°$, $-1.23°$, and $-1.85°$, respectively. Numerically, in the case of water, a lowering of the vapor pressure by $\frac{1}{100}$ of its amount at each temperature sets the freezing-point back 1.05°.

In everyday life we scatter salt on ice to melt it. The salt dissolves in the moisture on the surface, and the ice cannot exist in presence of this solution at 0°. It melts, absorbing heat in doing so, until the temperature of the mixture reaches that of a freezing, saturated solution of salt (about $-21° = -6°$ F.). When the existing temperature is lower than this, the salt has no effect on the ice. **Freezing mixtures**, being always mixtures of ice with various soluble substances, work in accordance with the principle.

Densities of Solutions. — The densities or specific gravities of solutions are also functions, although not simple ones, of the concentrations, and hence the latter are commonly defined for commercial purposes by the former. We purchase ammonium hydrate of "0.88 sp. gr.," meaning 35 per cent of ammonia, or sulphuric acid of "1.84 sp. gr.," meaning 100 per cent of the acid.

The solution usually has a smaller volume than that of the sum of the constituents. Thus, 58.5 g. of sodium chloride occupying 27.5 c.c., give, when dissolved in 10 liters of water, a solution whose volume is 10.0166 liters. The solution is only 16.6 c.c. more bulky than the water. Similarly, a formula-weight of potassium nitrate, occupying 44.7 c.c., adds only 38.5 c.c. to the bulk of 10 liters of water.

Heat of Solution. — When a body is dissolved in water, the solution may be either warmer or colder than the original materials. The

sources or destiny of the heat given out or absorbed have not been studied in such a way that definite statements can be made about the theory of the subject. There are many factors which would have to be considered. For example, the body, if a solid, goes into an essentially liquid condition, and its heat of fusion is always negative. The changes in its molecular condition involve either liberation or absorption of heat. The change in volume must have a heat effect connected with it. But almost nothing is known about these and other (see Heat of ionization) essential parts of the phenomenon.

The first water used always causes a greater heat change than the addition of succeeding equal amounts. Heats of solution are measured for the solution of one formula-weight of the substance in unlimited water. The values in calories for some common substances are as follows:

$(H_2SO_4, Aq) = +\ 39{,}170$	$(NaCl, Aq) = -\ 1180$
$(HCl, Aq) = +\ 17{,}400$	$(NH_4Cl, Aq) = -\ 3880$
$(KOH, Aq) = +\ 12{,}500$	$(KCl, Aq) = -\ 4440$
$(NaOH, Aq) = +\ 9780$	$(Na_2CO_3, 10H_2O, Aq) = -\ 16{,}160$
$(Na_2CO_3, Aq) = +\ 5640$	$(Na_2SO_4, Aq) = +\ 460$
$(CaCl_2, Aq) = +\ 3258$	$(Na_2SO_4, 10H_2O, Aq) = -\ 18{,}760$

When a substance comes out of solution, the heat effect is equal and of opposite sign to that occurring when the same substance goes into solution. Hence, since the decahydrate of sodium sulphate absorbs heat in dissolving, a considerable development of heat is noticed when it suddenly crystallizes from a supersaturated solution. Some ether in a tube immersed in the solution may be boiled by this heat and its vapor set on fire to make the fact evident at a distance. An important relation between heat of solution and solubility will be discussed under van't Hoff's law of mobile equilibrium (*q.v.*).

Definition of a Solution. — We are now able to make a brief statement which shall distinguish solutions from mixtures on the one hand and from chemical compounds on the other. **Solutions are homogeneous mixtures of two or more substances which are not separable into their constituents by mechanical means without altering the state of one of the substances, and whose properties vary continuously with the proportions of the constituents between certain limits.**

Application in Chemical Work. — The theory of this subject has been given on account of its intensely practical interest, and it

should be kept in mind in all ordinary chemical operations. It will afford an explanation of many things which might otherwise be attributed to the wrong cause, or might remain entirely without explanation. For example, why is the action of a metal upon an acid so slow? We must remember that an acid diluted with water is being used, and only one molecule out of every dozen or hundred is a molecule of the acid. So that the access of the latter to the metal is restricted at first, and becomes more and more so as the molecules of the acid in the immediate vicinity of the metal undergo chemical change.* On the other hand, the metal, especially if it be in the form of sticks obtained by casting, presents one of the elements in the action in a most compact form. The only parts which are accessible to the acid are those upon the surface, and, the metal not being appreciably soluble in water, the molecules can only pass off and expose a fresh layer very slowly. It is no wonder that many chemical actions occupy a considerable time. The wonder is that they should take place as rapidly as they do. Their speed would seem to point to a most intense chemical activity, even in the seemingly feebler instances. Various artifices are habitually employed for facilitating chemical action. Thus, the metal may be reduced to a leafy form by pouring the molten substance into cold water. Naturally, with metals, the maximum surface and the most rapid chemical action are obtained by using a fine powder.

The most speedy interaction of all, other things being equal, must be attainable by dissolving all the interacting substances in water. Under these circumstances all the molecules of each substance must simultaneously have many molecules of the others within easy reach of them.

Exercises. — 1. Give other examples of limited solubility in various solvents (p. 146).

2. If you were not permitted to evaporate sea-water to dryness, how should you show that it was a solution and not a pure substance?

3. Reëxpress Henry's law (p. 154) in terms of the volume of gas dissolved at different pressures.

4. If hydrogen sulphide is diluted with ten times its volume of hydrogen, what volume of it, estimated as pure gas, will be dissolved by 20 volumes of alcohol at 0° and 760 mm. (p. 154)?

* In spite of the continuous exhaustion of the acid, there is often a steady increase in the rate at which a dilute acid interacts with a metal. This is due, at first, to the dirt on the surface of the metal which temporarily obstructs the action, and, later, to the rising temperature of the interacting bodies.

5. If the dissolved air, after being removed from water by boiling, were to be shaken with water once more, in what proportions by volume would the gases now dissolve (p. 155)?

6. Read from the curves (p. 157) the solubilities of potassium nitrate at 15°, of potassium chloride at 30°, of potassium chlorate at 45°. What are the relative rates at which the solubilities of these salts increase with rise in temperature?

7. Express the concentrations of solutions of ammonium chloride, saturated at 0° (sp. gr. 1.076), and of potassium sulphate K_2SO_4, saturated at 10° (sp. gr. 1.083), in terms of a normal solution (p. 149).

8. Express the concentration of a five per cent aqueous solution of phosphoric acid (sp. gr. 1.027), in terms of a normal and a molar solution, respectively.

9. Name the phases (p. 156) in a system consisting of oxygen and its aqueous solution, (*a*) above 0°, (*b*) below 0°.

10. When a solution of a very soluble substance, like zinc chloride, is evaporated to dryness on a water bath, why is the escape of the last portions of the solvent so much slower than is that of the first?

CHAPTER XI

CHLORINE AND HYDROGEN CHLORIDE

CHLORINE was first recognized as a distinct substance by Scheele (1774). He obtained it from salt by means of manganese dioxide, using the common method described below. It was for years supposed to be a compound containing oxygen, but the work of Davy (1709–1818) established the fact that it is an element.

Occurrence. — Chlorine does not occur free in nature. There are, however, many compounds of it to be found in the mineral kingdom. Sea-water contains a number of chlorides in solution. Nearly 2.8 of the 3.6 per cent of solid matter in sea-water is common salt (sodium chloride, $NaCl$). During past geological ages the evaporation of sea-water has led to the formation of immense deposits of the compounds usually found in such water. Thus, at Stassfurt, such strata attain a thickness of over a thousand feet. Certain layers of these strata are composed mainly of sodium chloride, called by the mineralogist halite (rock salt). In other layers potassium chloride (sylvite), and hydrated magnesium chloride (bischofite), and other compounds of chlorine, occur. The chloride of silver (horn silver) is a valuable ore.

Preparation. — Chlorine cannot be obtained with the same ease as oxygen. There are only a few chlorides, such as those of gold and platinum, which lose chlorine when heated, and they are too expensive or difficult to make for laboratory use. We employ therefore methods like those used for the preparation of hydrogen. We may (1) decompose any chloride by means of electricity, just as, to get hydrogen, we electrolyzed a dilute acid (pp. 63, 94). Or (2) we may take some inexpensive compound of chlorine, such as hydrogen chloride (HCl), and by means of some simple substance which is capable of uniting with the other constituent, — here oxygen serves the purpose, — secure the liberation of the element (p. 99). Or (3) — and this turns out to be the most convenient laboratory method — we may use a more complex action.

Electrolysis of Chlorides. — Hydrogen chloride and those chlorides of metals which are soluble in water are all decomposed when a current of electricity is passed through the aqueous solution. They yield chlorine at the positive electrode. The other constituent, the hydrogen (Fig. 65), manganese, or whatever it may be, is liberated at the negative wire. To decompose hydrochloric acid an electromotive force of at least 1.31 volts is required. Since the chlorine is soluble in water, the effervescence due to its release is not noticeable until the liquid round the electrode has become saturated with the gas: Cl_2 (diss'd) $\rightleftarrows$ Cl_2 (gas). The shape of the apparatus keeps the two products from mingling. The presence of the chlorine in the liquid at the positive end may be shown by a suitable test (pp. 99 and 175).

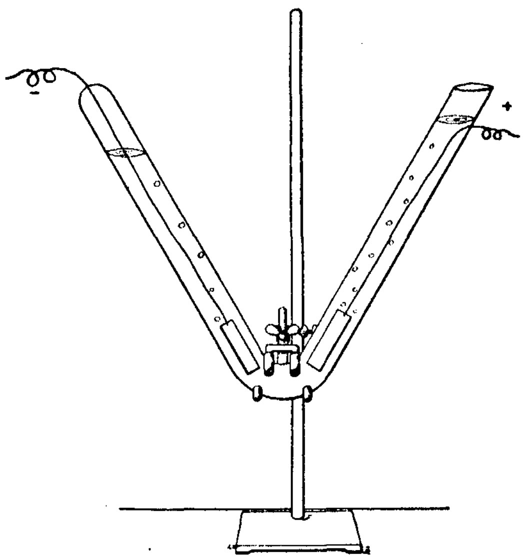


FIG. 65.

In commerce chlorine is now obtained chiefly by this method, sodium chloride or potassium chloride being the source of the element. Electrodes of artificial graphite are used, as most other conductors unite with the chlorine. The potassium or sodium, as the case may be, travels towards the negative electrode, but is not liberated (p. 99). Instead, potassium or sodium hydroxide accumulates in the solution round the plate and hydrogen escapes. The chlorine is released at the positive electrode, as usual. The hydroxide and the chlorine both find chemical applications. The chlorine is either liquefied by compression in iron cylinders or employed at once for making bleaching powder (*q.v.*).

In the Acker process (*q.v.*), melted, impure sodium chloride, without any solvent, is electrolyzed.

Action of Free Oxygen on Chlorides. — Oxygen does not interact with sodium chloride even at a high temperature. Hence the chlorine must first be transferred to some other form of combination. By the interaction of acids, of which the most commonly used is sulphuric acid, with chlorides, of which the cheapest is sodium chloride, we obtain hydrogen chloride. The details of this action are described below (p. 178). In order to liberate chlorine from this compound, we may combine the hydrogen with oxygen obtained from the air. The action is in accordance with the equation:

$$2HCl + O \rightarrow H_2O + 2Cl.$$

The two gases interact so slowly, however, that a catalytic agent must be employed. The mixture of air and hydrogen chloride is passed over pieces of heated pumice-stone or broken brick previously saturated with cupric chloride solution. A temperature of 370°–400° is used. In the resulting gas the chlorine is mixed with steam and with a very large volume of nitrogen which entered with the oxygen, so that for making the pure substance this method (Deacon's process) is quite unsuitable.

Using the same principle, magnesium chloride may be heated in a stream of air, when the oxide of magnesium is formed and chlorine is given off: $MgCl_2 + O \rightarrow MgO + 2Cl$. The oxide of magnesium can then be treated with hydrochloric acid to regenerate the chloride, which in turn may be subjected once more to the action of oxygen. The process is thus a continuous one.

The above action is spoken of as an oxidation. It is true that no oxygen is actually introduced into the hydrogen chloride as a whole. The removal of hydrogen from combination with the chlorine is, however, the first step towards the introduction of oxygen into combination with the latter, and is essentially an oxidation.

Action of Combined Oxygen upon Chlorides. — The usual laboratory method of making chlorine is to mix a solution of hydrogen chloride in water (hydrochloric acid, p. 93) with roughly powdered manganese dioxide. The flask containing the mixture is heated by means of a bath containing hot water (Fig. 66). The gas is passed through a washing bottle containing water, in order to remove some hydrogen chloride which may be carried over. It may be dried, if necessary, in a second washing bottle containing concentrated sulphuric acid. It cannot be collected over water on account of its solubility, so that jars are usually filled with it by downward displacement of air.

The chemical change used here is somewhat complex. When an acid (here HCl) interacts with an oxide (here MnO_2), the hydrogen of the former unites with the oxygen of the latter, giving water. We perceive at once that to combine with 2O, 4H, obtainable only by taking 4HCl, will be required. Hence the equation might be :

$$MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_4.$$

This is probably what happens in the first place. The products actually obtained, however, are water, manganous chloride ($MnCl_2$) and

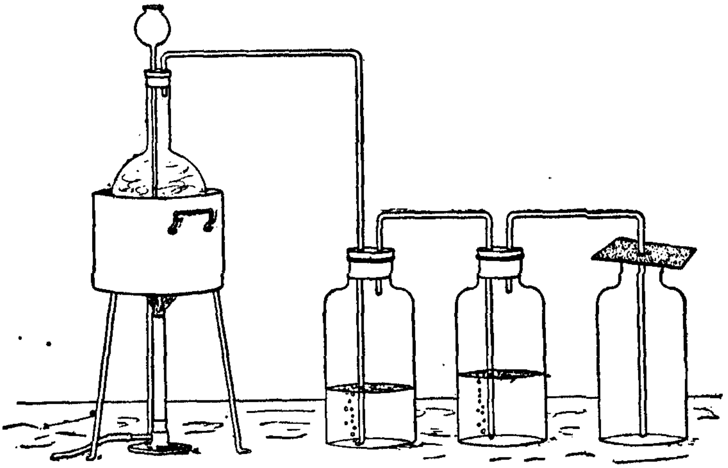


FIG. 66.

chlorine. The manganese tetrachloride is decomposed by the heating, the chlorine escapes, and the other two products remain in the vessel.

$$MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_2 + 2Cl. \qquad (1)$$

We owe the chlorine to the fact that the tetrachloride is unstable.

When the mixture is surrounded by ice and saturated with chlorine, it can be shown with some degree of certainty that it contains the tetrachloride. If it is quickly poured into water, hydrated manganese dioxide is precipitated (Wacker). The decomposition of the tetrachloride is reversible :

$$MnCl_4 \rightleftarrows MnCl_2 + Cl_2,$$

and is driven back by the excess of chlorine. The tetrachloride is hydrolyzed by water :

$$MnCl_4 + 2H_2O + xH_2O \rightarrow MnO_2, xH_2O + 4HCl.$$

The action (1) is of a type very common in chemistry. It is more complex even than double decomposition (p. 99), and, unlike this, its results cannot be anticipated by guessing. If we had used manganous oxide (MnO), we should have had a double decomposition:

$$MnO + 2HCl \rightarrow H_2O + MnCl_2, \qquad (2)$$

but we should have got no chlorine. Perhaps the simplest way to describe the difference between these two actions is in terms of the valence of the manganese. In $Mn^{IV}O_2{}^{II}$ the element is quadrivalent. This means that its atomic weight professes to be able to hold four unit weights of a univalent element. The four valences of oxygen ($2O^{II}$) can do the same thing. In equation (1) the oxygen fulfils this promise by taking $4H.^{I}$ But the Mn^{IV} can hold only $2Cl^{I}$ permanently and lets the other $2Cl^{I}$ go free. In other words, the *valence* of the unit weight of *manganese changes* in the course of the action. In equation (2), on the other hand, the manganese is bivalent to start with ($Mn^{II}O^{II}$), and is able to retain the amount of chlorine ($2Cl^{I}$) equivalent to O^{II}. Actions like that of manganese dioxide in (1) are classed as oxidations. The hydrogen chloride, or rather half of it, is oxidized. A graphic mode of writing may make this remark clearer:

$$Mn^{IV}\begin{matrix} \nearrow O + 2HCl \rightarrow H_2O + Mn^{II}Cl_2 \\ \searrow O + 2HCl \rightarrow H_2O + 2Cl. \end{matrix}$$

The upper half is a double decomposition, the lower an oxidation by half the combined oxygen of the dioxide.

In practice, instead of employing aqueous hydrochloric acid we frequently use the materials from which it is prepared, namely, common salt and concentrated sulphuric acid (p. 178), along with the manganese dioxide. Under those circumstances, the action appears more complex, but is simply a combination of the two chemical changes, and is represented by the equation:

$$MnO_2 + 2NaCl + 3H_2SO_4 \rightarrow 2H_2O + 2NaHSO_4 + MnSO_4 + 2Cl.$$

Using the same principle, we find that lead dioxide, barium dioxide, potassium dichromate ($K_2Cr_2O_7$), potassium permanganate ($KMnO_4$), and many other substances, when treated with aqueous hydrochloric acid, likewise give chlorine.

Perhaps the best way to obtain a steady, easily regulated stream of chlorine is to place some solid potassium permanganate in a flask, arranged like that in Fig. 70 (p. 232) but without the U-tubes, and

allow concentrated commercial hydrochloric acid, diluted with half its volume of water, to fall upon it drop by drop from the dropping funnel. The action is very rapid, the acid is exhausted almost as fast as it falls, and so the stream of gas can be stopped by simply closing the stopcock. In this, and in all the cases mentioned above, the chemical action follows the same plan as before (p. 171). The oxygen and hydrogen combine to form water, hence here 8HCl will be needed; the metals yield the chlorides which are stable at the temperature of the action, and the rest of the chlorine is liberated:

$$KMnO_4 + 8HCl \rightarrow 4H_2O + KCl + MnCl_2 + 5Cl.$$

Kinetic-Molecular Hypothesis Applied to these Actions. — In preparing chlorine by the usual laboratory method (p. 170), it will be observed that the gas is produced rather slowly. Even heating does not accelerate the interaction very greatly. The situation is that we have placed together manganese dioxide in a granular form and water which contains hydrogen chloride in solution. The dioxide is very insoluble in water, and consequently its molecules, which must dissolve before they can meet the acid, become available very slowly: MnO_2 (solid) $\rightleftarrows$ MnO_2 (diss'd). The finer the pulverization, the less will be the delay from this cause. On the other hand, the acid contains originally only about one molecule of hydrogen chloride for every four of water, and as the former is used up the scarcity of the active substance becomes greater.

Again, we heat the mixture on a water bath so as to hasten the process (p. 72) by raising the temperature to about 90°. When we prepared oxygen, we forced the temperature up with a naked Bunsen flame until, between 200° and 300°, a sufficiently rapid stream of the gas was secured. The iron and sulphur (p. 11) we raised nearly to a red heat. Here the conditions make stronger heating impossible. No aqueous solution of hydrogen chloride can be raised above 110°, the maximum boiling-point (p. 182). But we must not carry the heating so far as 110°, because even below this point the concentrated acid gives off gaseous hydrogen chloride freely. If we did, we should contaminate our chlorine and at the same time lose a part of one of the ingredients on which the action depends. Intelligent chemical work always demands a careful consideration of purely physical facts of this description.

Physical Properties. — Chlorine differs from the gases we have encountered so far in having a strong greenish-yellow tint (Gk.

χλωρός, pale green), a fact which gave rise to its name, and having a powerful irritating effect upon the membranes of the nose and throat.

Density (H = 1), 35.79	Boiling-point (liq.), − 33.6°
Weight of 1 l., 3.220 g.	Melting-point (solid), − 102°
Solubility in Aq. (20°), 215 vols. in 100	Vap. tension (liq.) 0°, 3.66 atmos.
Crit. temp., + 146°	Vap. tension (liq.) 20°, 6.62 atmos.

Since a liter of air weighs 1.293 g., chlorine is two and a half times heavier. In solubility it stands between slightly soluble gases, like oxygen and hydrogen, and those which are extremely soluble. It can be collected over hot water or a strong solution of salt.

It was first liquefied by Faraday. The critical temperature (p. 133) is exceptionally high (146°), so that at all ordinary temperatures the gas can be liquefied by compression alone. It forms a yellow liquid which, contained in steel cylinders, is now an article of commerce. On being cooled below − 102°, it gives a pale-yellow solid.

Chemical Properties. — Chlorine is at least as active a substance as is oxygen. It presents a more varied array of chemical properties than does that element.

1. When a strong solution of chlorine in water is cooled with ice, crystals of chlorine hydrate ($Cl, 4H_2O$) are formed. This hydrate, being the hydrate of a gas, has a high vapor tension of chlorine, as well as a smaller one of water (p. 121). At 0° the partial tension of the chlorine is 249 mm., at 9.6° it is 760 mm. The compound decomposes rapidly, therefore, at the latter temperature unless the pressure of chlorine over it is greater than one atmosphere.

2. Chlorine **unites directly with many elements.** A jet of hydrogen burns vigorously in chlorine, producing hydrogen chloride. The presence of this product may be recognized at once, because, while chlorine in contact with moist breath gives no cloud, hydrogen chloride (*q.v.*) produces a dense fog. The union of the gases, when a mixture of them is kept cold and in the dark, is too slow to be perceived. On exposure to diffused light, however, they unite slowly, while a sudden flash of sunlight or the burning of a magnesium ribbon causes instant explosion. The function of the light here is entirely different from that in the decomposition of silver chloride (p. 19). In the latter case light was used to maintain the change, which comes to a stop whenever the light is withdrawn. The action was endothermal and consumed energy. The union of hydrogen and chlorine is highly exothermal, and a minimum of light only is needed to start it (p. 74).

Sodium burns in chlorine, producing a cloud of white particles of sodium chloride. Copper in the condition of thin leaf commonly used for gilding (Dutch-metal), catches fire spontaneously when thrust into the gas. Phosphorus burns in it with a rather feeble light, producing phosphorus trichloride, a liquid (b.-p. 74°) which condenses readily. The proportions of the materials taking part in this change show that one atomic weight of phosphorus (31) and three atomic weights of chlorine form the product:

$$P + 3Cl \rightarrow PCl_3.$$

Almost all the more familiar elements unite directly with chlorine to form chlorides. The exceptions are, nitrogen, oxygen, carbon, helium, and argon (p. 68). Compounds with all but the last two may be obtained as products of more complex interactions, however.

Some elements form more than one chloride. Thus, when phosphorus unites at a high temperature with chlorine, we get phosphorus trichloride. When we pass chlorine gas into cooled phosphorus trichloride, however, a considerable absorption takes place, and finally a solid body containing two more atomic weights of chlorine, phosphorus pentachloride (PCl_5), is formed.

Carefully dried substances unite slowly or, to all appearances, not at all with chlorine. Thus, perfectly dry chlorine does not unite with copper, even when the system is warmed. The introduction of a drop of water (p. 75), however, into a remote part of the apparatus at once supplies the trace of moisture which seems to be necessary to start the chemical change. Chlorine, as ordinarily made, unites with iron with great vigor. But dried chlorine is quite indifferent and does not attack the steel cylinders in which it is now sold. The water is a catalytic agent, and we regard it as simply hastening an action which otherwise is vanishingly slow (p. 73).

3. Chlorine, like sodium (p. 97), **may also displace elements which are already in combination**. Thus, when turpentine ($C_{10}H_{16}$) is poured over a strip of paper and is then immersed in a jar of chlorine, a violent action takes place, and an immense cloud of finely divided carbon bursts forth. The heat of the action, as it starts, vaporizes the turpentine, and the hydrogen in the latter unites with the chlorine forming hydrogen chloride, while the carbon is set free: ($C_{10}H_{16}$ + $16Cl \rightarrow 16HCl + 10C$).

The action of chlorine on potassium iodide, dry or in solution, is of this kind, and furnishes the commonest **test** (p. 99) **for free chlorine**.

The chlorine simply takes the place of the iodine ($KI + Cl \rightarrow KCl + I$), and the latter is liberated. Iodine when moist is deep brown in color, and the amount liberated by a large quantity of chlorine may easily be seen. Yet, it is an advantage so to arrange a test that it may be as **delicate** as possible, that is, may give a plainly visible result with the minimum of material. In this case much starch emulsion and a little potassium iodide are employed. Strips of filter paper dipped in this mixture show a deep-blue color (see Iodine) when brought into a gas containing even a trace of free chlorine. Combined chlorine, as in a chloride, has no effect.

4. When actions like the above are moderated by proper means, the decomposition is not so complete. If methane (marsh gas, CH_4) is mixed with chlorine and exposed to sunlight, a slower action occurs, of which the first stage consists in the removal of one unit weight of hydrogen and the **substitution** of chlorine for it according to the following equation:

$$CH_4 + 2Cl \rightarrow CH_3Cl + HCl.$$

The process may continue further by the substitution* of chlorine for the units of hydrogen one by one until carbon tetrachloride (CCl_4) is finally formed.

A most interesting and important action of this class occurs when chlorine is dissolved in water. A small part of the chlorine interacts with a little of the water, the element being substituted for one-half of the hydrogen:

$$2Cl + HHO \rightarrow HOCl + HCl. \qquad (1)$$

Only *traces* of hydrogen chloride and hypochlorous acid are produced, however. The change comes quickly to a standstill, because the products interact even more vigorously to reproduce chlorine and water:

$$HCl + HOCl \rightleftarrows 2Cl + H_2O, \qquad (2)$$

the interaction being reversible (p. 64). This interaction of chlorine and water (1), slight as it is, is of importance on account of the insta-

* **Substitution** resembles displacement (p. 99) in that an element and a compound interact, and the element takes the place of one unit in the composition of the latter. In the above action, one unit of chlorine takes the place of one unit of hydrogen. But the latter is not liberated: it combines with another unit of chlorine. *Double* decomposition the action is not, because elements do not decompose. The name used is intended to fix the attention on the *compound* and on the fact that one unit has been *substituted* for another in it. This conception is a favorite one in the chemistry of compounds of carbon.

bility of the hypochlorous acid (*q.v.*) which it produces. When the solution is exposed to sunlight, the hypochlorous acid decomposes and oxygen gas is produced: $HClO \rightarrow HCl + O$. Since this removes the substance on whose interaction with the hydrogen chloride in (2), the reversal of (1) depends, the latter action proceeds under continuous illumination gradually to completion. Hence the aqueous solution of chlorine must be kept in the dark, since otherwise a dilute solution of hydrogen chloride alone remains.

The so-called bleaching action of "chlorine" is almost always the result of oxidation of the coloring matter by hypochlorous acid. Chlorine and the dye in the cloth, even when only moderately dry, show no tendency to interaction. This may be demonstrated by collecting some chlorine in a stoppered bottle in the bottom of which a little concentrated sulphuric acid stands. A piece of colored calico may be attached by a pin to a cork stuck in the bottom of the stopper and so suspended in the gas. After twenty-four hours no action will be found to have occurred. Yet if the rag is first moistened, the bleaching is almost instantaneous. Hence this bleaching action is treated under the properties of hypochlorous acid.

5. Chlorine may simply add itself to a compound. Thus, one of the oxides of carbon, carbon monoxide (CO), when mixed with chlorine and exposed to sunlight gives drops of a volatile liquid (b.-p. 8.2°) known as phosgene ($COCl_2$).

Chemical Relations of the Element.* — In the formation of chlorides, an atomic weight of chlorine is equivalent to one atomic weight of hydrogen or of sodium. The element is, therefore, univalent (p. 103). It never shows any higher valence than this save in its oxygen compounds (see Chap. xvi). The oxides of chlorine interact with water to give acids, and the element is, therefore, to be classed as a non-metal (p. 119). It belongs to that group of the non-metals called the halogens (*q.v.*), as a consideration of some others of its relations will show (see Chap. xiv).

Uses of Chlorine. — Large quantities of chlorine are manufactured for the preparation of bleaching materials and disinfecting agents.

* In accordance with the distinction that must be drawn (p. 32) between the element as a variety of matter in combination, and the elementary substance or free form of the element, and to avoid a common source of confusion, we shall always give only the behavior of the elementary *substance* under the title *chemical properties*. The characteristics which distinguish the *compounds* of the element, as a class, from, or relate them as a class to the compounds of other elements will then appear in a separate section under the above title (see Chap. xiv, first section).

In disinfection, the minute germs of disease and putrefaction are acted upon either by the chlorine or by the hypochlorous acid formed by its interaction with water, and instantly their life is destroyed. One of the processes for the extraction of gold involves an action of chlorine gas upon the material after it has received preliminary treatment. A chloride of gold is formed, which can be dissolved out of the matrix by means of water, and the metallic gold is afterwards precipitated from the solution.

Hydrogen Chloride.

Preparation from Sodium Chloride. — As we have seen, the direct union of hydrogen and chlorine produces a gas, hydrogen chloride (HCl). For the purpose of preparing this gas, however, some more easily managed method will naturally be employed.

In commerce large quantities of hydrogen chloride are obtained as a by-product in connection with the manufacture of soda. The same materials are commonly employed in the laboratory. Common salt is treated with concentrated sulphuric acid at a gentle heat. Effervescence is seen and hydrogen chloride is given off, while a compound known as sodium hydrogen sulphate (sodium bisulphate) remains behind. The action is represented by the equation:

$$NaCl + H_2SO_4 \rightarrow HCl \uparrow + NaHSO_4. \qquad (1)$$

The apparatus used in the preparation of chlorine (Fig. 66) may be employed. On account of its extreme solubility the gas is not washed in water, however. For the same reason it must be collected by downward displacement of air, or over mercury.

The above statements apply to the action of a large amount of sulphuric acid upon a limited amount of salt, where no high temperature is employed. If, however, a larger proportion of salt is used and a sufficiently high temperature produced by artificial heating, then common sodium sulphate is formed according to the equation:

$$2NaCl + H_2SO_4 \rightarrow 2HCl + Na_2SO_4. \qquad (2)$$

The former action is that which occurs under the conditions used in the laboratory. The latter is the action which is employed in commerce, since it is for the purpose of making sodium sulphate (Na_2SO_4), from which sodium carbonate is afterwards to be prepared, that the operation is undertaken. The hydrogen chloride passes through a tower, down which water trickles over lumps of coke, and is dissolved.

The aqueous solution is called hydrochloric acid, or, in commerce, muriatic acid.

Interaction of Acids and Chlorides. — It should be noted that the above is simply an illustration of a perfectly general method. Almost any chloride of a metal might have been used instead of sodium chloride, and almost any acid which could be obtained *free from* any large amount of *water* (see below) could have taken the place of sulphuric acid. Thus, concentrated phosphoric acid with any chloride will give a change parallel to the above. With sodium chloride this action would be $NaCl + H_3PO_4 \rightarrow HCl\uparrow + NaH_2PO_4$ (primary sodium phosphate).

If various chlorides are used with the same acid, it will be found that the vigor of the actions is very different. In some, hydrogen chloride will be produced copiously without the assistance of heat. In others, there will be difficulty in showing that hydrogen chloride gas is produced at all. We must not hastily assume that this is owing to any greater chemical affinity in one case than another. More extensive experimentation will show that the *more soluble* chlorides as a rule give more vigorous effects than those which are less so (pp. 166, 173). Ammonium chloride with sulphuric acid would represent the former variety, while mercuric chloride with the same acid would represent the latter.

The Kinetic Hypothesis Applied to the Interaction of Sulphuric Acid and Salt. — One who has used the above method for making hydrogen chloride without reflection would not realize the complexity of the machinery by which the result is achieved. The means are apparently very simple. Yet the mechanical features of this experiment, when laid bare, are extremely curious and interesting. A single fact will show the possibilities which are concealed in it.

If we take a saturated solution of sodium hydrogen sulphate in water and add to it a concentrated solution of hydrogen chloride in water (concentrated hydrochloric acid), we shall perceive at once the formation of a copious precipitate. This is composed entirely of minute cubes of sodium chloride:

$$NaHSO_4 + HCl \rightarrow H_2SO_4 + NaCl\downarrow. \qquad (3)$$

Now this action is nothing less than the precise reverse of (1), yet it proceeds with equal success. In fact, this chemical interaction is not only reversible (p. 64), but can be carried to completion in either direc-

tion. It is only in presence of a large amount of water that it stops midway in its career and is valueless for securing a complete transformation in either direction :

$$NaHSO_4 + HCl \rightleftarrows H_2SO_4 + NaCl.$$

In an action which is reversible, if the products remain as perfectly mixed and accessible to each other as were the initial substances, their interaction will continually undo a part of the work of the forward direction of the change. Hence, in such a case the reaction must, and does, come to a standstill while as yet only partly accomplished (*cf.* p. 176); but this was not the case with actions (1) and (3). Let us examine the means by which the premature cessation of each was avoided.

In (1) the salt dissolved to some extent in the sulphuric acid, NaCl (solid) $\rightleftarrows$ NaCl (diss'd), and so, by contact of the two kinds of molecules, the products were formed. On the other hand, the hydrogen chloride, being insoluble in sulphuric acid, escaped as fast as it was formed: HCl (diss'd) $\rightleftarrows$ HCl (gas). Hence, in that case, almost no reverse action was possible, and the double decomposition went on to completion. With all the sodium hydrogen sulphate in the bottom of the flask, and most of the hydrogen chloride in the space above, the two products might as well have been in separate vessels so far as any efficient interaction was concerned. This plan, in which water is purposely excluded, forms therefore the method of making hydrogen chloride.

In (3), on the other hand, the hydrogen chloride was taken *in aqueous solution*, and was kept permanently in full contact with the sodium bisulphate. It had therefore in this case every opportunity to interact with the latter and no chance of escape. Every molecule of each ingredient could reach every molecule of the other with equal ease. Furthermore, the sodium chloride produced as a result of their activity is not very soluble in concentrated hydrochloric acid (far less so than in water), and so it came out as a precipitate: NaCl (diss'd) $\rightleftarrows$ NaCl (solid). But this was almost the same as if it had gone off as a gas. It meant that the greater part of the salt was in the solid form. It was in a state of fine powder, it is true. But, in the molecular point of view, the smallest particle of a powder contains millions of molecules, and most of these are necessarily buried in the interior. Thus the sodium chloride was no longer able to interact effectively molecule to molecule with the other product, the sulphuric

acid. Hence, there was little reverse action to impede the progress of the primary one. Thus (3) is nearly as perfect a way of liberating sulphuric acid as (1) is of liberating hydrogen chloride.

This discussion is given to show that, in many chemical actions, the affinity is entirely subordinated by the effects of a purely mechanical arrangement (*cf.* pp. 28, 110, 166). If the latter is well devised, an action propelled by a feeble affinity may prevail against a reverse action involving a very powerful one (see Chemical equilibrium).

The egregious misconception that sulphuric acid is shown by this action to be "stronger" than hydrochloric acid was disposed of, so far as the science was concerned, half a century ago. But it survives in suburban chemical circles with remarkable tenacity. The fact, quaintly enough, is that the real relation in respect to activity is just the reverse.

Other Ways of Obtaining Hydrogen Chloride. — Although never used for generating hydrogen chloride on a large scale, there is another important kind of action in which the substance is a product. When water acts upon the chlorides of non-metallic substances like sulphur, phosphorus, and iodine, a double decomposition occurs. Since water is always one of the interacting substances, this kind of change, — **a double decomposition involving water,** — is called **hydrolysis** (Gk. ὕδωρ, water, and λύσις, the act of loosing). Thus, when a little water is added to one of the chlorides of phosphorus, hydrogen chloride is formed. Besides this, the trichloride gives phosphorous acid, and the pentachloride, phosphoric acid:

$$PCl_3 + 3HOH \rightarrow 3HCl + P(OH)_3,$$
$$PCl_5 + 4H_2O \rightarrow 5HCl + H_3PO_4.$$

A dissociation is a reversible decomposition of one substance into two. Hydrolysis is an ordinary double decomposition or metathesis where water is one of the reagents. Yet it has been perversely named **hydrolytic dissociation** by many writers. A whole chapter might be devoted to the ingenuity with which chemists have misnamed many of the things with which they deal. Perhaps this tendency is a survival of the habit the chemists had of using obscure and symbolical names for their materials to prevent the penetration of their secrets by uninitiated seekers after knowledge. Important facts and principles have been sedulously labeled with misleading titles, like: Water of crystallization, which has no more to do with crystallization than with color, density, or any other physical property; supersaturated solution, which, as a solution, is the same as any other; mass action, which has nothing to do with mass, but is concerned wholly with concentration; strong acid, which refers to activity and not power of resistance; reciprocal proportions, a law in which reciprocals of numbers play no part; downward displacement of air, when the air is displaced upwards, and so forth. Here there

is an opportunity to confuse hydrolysis with electrolytic dissociation, and the beginner never fails to embrace it. Hydrolytic double decomposition would have been a correct if somewhat clumsy term.

Often, when a steady stream of hydrogen chloride is required, concentrated hydrochloric acid is placed in a generating flask, and concentrated sulphuric acid is allowed to trickle into it from a dropping funnel. The hydrogen chloride is less soluble in diluted sulphuric acid than in water (see Product of solubility) and escapes.

Physical Properties. — Hydrogen chloride is a colorless gas, which produces a suffocating effect when breathed.

Density (H = 1), 18.23	Crit. temp., + 52°
Weight of 1 l., 1.641 g.	Boiling-point (liq.), − 83.7°
Solubility in Aq. (0°), 50,300 vols. in 100	Melting-point (solid), − 110°

The gas is one-fourth heavier than air. On account of its great solubility and the small vapor tension of its solution, it condenses atmospheric moisture into a fog of drops of hydrochloric acid. On account of its high critical point, it may be liquefied by pressure alone. Both in the gaseous and liquefied states it is a nonconductor of electricity. Its heat of solution (p. 164) is 17,400 calories.

On account of its high concentration, the solution may be looked upon as a mixture of liquefied hydrogen chloride and water. At 15° and 760 mm. 454.6 volumes of the gas dissolve in 1 volume of water, or 746 g. in 1 l. The mixture weighs therefore 1746 g. (42.7 per cent of HCl). Its sp. gr. is 1.215. The volume of the solution is given by the proportion $1215 : 1 :: 1746 : x$, in which $x = 1.437$ l. Hence the addition of 454.6 liters of the gas has increased the volume by only 437 c.c. Now at 15° the sp. gr. of liquefied hydrogen chloride is 0.8320, and the volume of 746 g. is therefore $746 \div 0.832 = 896$ c.c. So that even if the substances had been mixed in liquid form a considerable shrinkage would still have occurred.

When the concentrated aqueous solution is heated, it is the gas and not the water which is driven out for the most part. When the concentration has been reduced to 20.2 per cent the rest of the mixture distils unchanged at 110°. If a dilute solution is used, *water* is the chief product of distillation (about 100°), but gradually the boiling-point rises, and, when the concentration has reached 20.2 per cent once more, the same hydrochloric acid of **constant boiling-point**, as it is called, forms the residue. It is thus impossible to separate by distil-

lation the components of mixtures which behave in this way. This must necessarily be the case whenever, as here, the vapor tensions of the components separately and those of all other mixtures are higher than that of one particular mixture. When, as is more often the case, one of the components has a vapor tension which is lower than that of the other and lower than that of any mixture of the two, this component will tend to remain behind, and separation can be effected. The separation of petroleum products (*q.v.*) from one another illustrates the common case (see under Alcohol for the third possibility).

The composition of the mixture having the minimum vapor tension varies with the external pressure, and so does the boiling-point. At 300 mm. the constant boiling liquid contains 21.8 per cent of hydrogen chloride and boils at 84°; at 1520 mm. it contains 19.1 per cent of the gas.

The common belief that hydrochloric acid of constant boiling-point is a definite compound is without foundation. Compounds do not vary in composition with changes in pressure in this manner. Aqueous solutions of hydrogen iodide, hydrogen bromide, and nitric acid behave in the same way. But solutions of oxygen, of ammonia, and of many liquids (*e.g.* alcohol) in water belong to the second of the two classes mentioned above, and the more volatile component often leaves the water entirely before much of the latter has evaporated.

Chemical Properties. — This compound is extremely stable, as we might expect from the vigor with which the elements of which it is composed combine. On being heated to a temperature of 1800° it begins, however, to dissociate into its constituents.

In the chemical point of view, it is on the whole rather an indifferent substance. When water is saturated with the gas at − 22° a hydrate ($HCl, 2H_2O$) crystallizes out. This decomposes into the same constituents when allowed to warm up again to − 18°. Hydrogen chloride (the gas) has no action upon any of the non-metals, such as phosphorus, carbon, sulphur, etc. Many of the metals, however, particularly the more active ones, such as potassium, sodium, and magnesium, decompose it. Hydrogen is set free, and the chloride of the metal is formed ($K + HCl \rightarrow KCl + H$). Hydrogen chloride unites directly with ammonia gas to form solid ammonium chloride ($HCl + NH_3 \rightarrow NH_4Cl$). The liquefied gas has the same properties.

Composition. — The proportion of hydrogen to chlorine by weight in this compound is 1 : 35.18. Taking the atomic weight of hydrogen 1.008, so as to harmonize that of chlorine with O = 16, the ratio becomes 1.008 : 35.45.

The proportion by volume in which the constituents unite, and the relation of this to the volume of the resulting hydrogen chloride, may easily be shown in several ways. The decomposition of the solution of hydrogen chloride in water by means of the electric current proves that the gases are liberated in equal volumes.

The apparatus in Fig. 31 (p. 94) cannot be used to show this, because, under the increasing pressure due to the displacement of the liquid into the higher bulb, the chlorine becomes more and more soluble, and its volume therefore falls progressively more and more below what it should be.

A special form of apparatus (Fig. 67) was devised by Lothar Meyer to demonstrate the volumetric proportion. The central part is the same as in Fig. 31, but the gases go to right and left, and displace the liquid in two inverted tubes. The equal rate at which this takes place on both sides proves that the gases are generated in equal volumes.

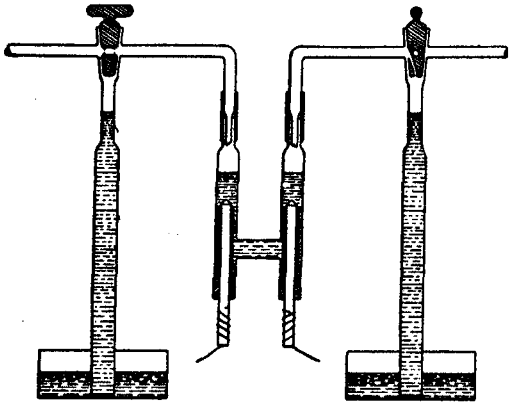


FIG. 67.

In order to ascertain the relation between the volumes of the constituents and that of the product, we may unite the gases and find out whether any change in volume occurs. A tube with thick walls (Fig. 68) is filled with the mixed gases obtained by electrolysis. By dipping one end of the tube under mercury and opening the lower stopcock, it is seen that no gas leaves and no mercury enters. After the mixture has been exploded, by the light from burning magnesium, the same test is repeated with the same result. The pressure has therefore remained equal to that of the atmosphere. Hence there has been no change in volume as the result of the union. It appears therefore, that:

1 vol. hydrogen + 1 vol. chlorine $\rightarrow$ 2 vols. hydrogen chloride,
a result in harmony with Gay-Lussac's law (p. 125).

Another way of demonstrating the equality in the volumes of the hydrogen and chlorine is to fill a wide tube, closed at each end by a stopcock, with the mixed gases arising from electrolysis of hydrochloric acid. When the air has been entirely displaced, the stopcocks are closed. The gases which the tube then contains are present very nearly in the proportions in which they are liberated from the decomposition of the substance. By introducing a small amount of potassium iodide solution, the chlorine is removed. It forms potassium chloride, which remains dissolved in the water, and free iodine, which dissolves in the excess of potassium iodide solution ($KI + Cl \rightarrow KCl + I$). Neither product is gaseous under the circumstances, so that the volume of the mixed gases diminishes by the amount of chlorine removed. If the stopcock is now opened under water, the latter enters and fills half the length of the tube. The remaining gas is easily shown to be hydrogen.

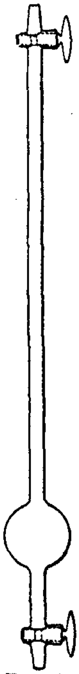


FIG. 68.

To show that the volume of the hydrogen chloride is twice that of either constituent in the free condition, an alternative method is likewise available. We may completely fill a long test-tube with hydrogen chloride, introduce into it quickly some sodium dissolved in mercury, and, after agitation, open the closed tube under mercury. The sodium gives sodium chloride and free hydrogen, and it is found that the mercury enters so as to fill one-half of the tube. Since from this experiment we learn that the hydrogen occupies half the space of the hydrogen chloride, and from the previous experiment we know that the volume of hydrogen is equal to that of the chlorine, we conclude that two volumes of mixed hydrogen and chlorine would give two volumes of hydrogen chloride.

Chlorides. — The chlorides are described individually under the other element which each contains. For the present we simply add to the statement on p. 179 that the majority of the chlorides which do not interact with water (p. 181), that is to say of the chlorides of the metals, are easily soluble in water. The only exceptions are silver chloride ($AgCl$), mercurous chloride (calomel, $HgCl$), cuprous chloride ($CuCl$), aurous chloride (one of the chlorides of gold, $AuCl$), thallous chloride ($TlCl$), and ordinary lead chloride ($PbCl_2$). The last of these is on the border line as regards solubility. An appreciable amount dissolves in cold water, and a considerable amount in boiling water.

Chemical Properties of Hydrochloric Acid. — The solution of hydrogen chloride in water is an entirely different substance in its chemical behavior from hydrogen chloride. It is strongly acid, turning litmus red. The gas and liquefied gas have no such property. The solution conducts electricity, as we have seen, very well, and is decomposed in the process (*cf.* p. 194).

Many metals, when introduced into hydrochloric acid, displace the hydrogen (p. 95), and form the chloride of the metal. In the case of zinc the action was represented by the equation:

$$Zn + 2HCl \rightarrow ZnCl_2 + 2H.$$

The liquefied gas has no action upon zinc, and even its solution in many solvents shows little activity. The solution in alcohol behaves like that in water. But the solutions in toluene, benzene, and other compounds of carbon and hydrogen, in many of which the gas is freely soluble, are hardly affected by the presence of zinc and other metals. These, and many other facts which we shall notice later (see Dissociation in solution), show that the condition of this substance in aqueous solution is peculiar.

The aqueous solution of hydrogen chloride interacts rapidly with most oxides and hydroxides, as, for example, those of zinc:

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O,$$
$$Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O.$$

Here no free hydrogen is obtained, since the oxygen in the oxide, and the hydroxyl in the hydroxide, unite with it to form water. In each case, however, the chloride of the metal is obtained. It may be noted in passing that all acids behave in a similar manner towards oxides and hydroxides, giving water and a compound corresponding to the chloride (*cf.* p. 171). Dilute sulphuric acid, for example, gives sulphates.

In the two preceding paragraphs, three kinds of actions, each constituting a different way of obtaining chlorides, have been mentioned incidentally. There are two others which we have already encountered. The simplest is the direct union of the element with chlorine ($Zn + 2Cl \rightarrow ZnCl_2$). The other method is illustrated in the case of the precipitation of silver chloride (p. 13). Here the formation of the chloride occurred by exchange of another radical for chlorine ($AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$). The insoluble chlorides (p. 185) can be made conveniently by this plan. The formation of the precipitates, for example that of silver chloride, is used as a test for the presence of a soluble chloride in the solution.

The solution of hydrogen chloride in water sold in commerce is known by the name of muriatic acid (Lat. *muria*, brine). It is a yellow liquid which contains a number of impurities. The most common are ferric chloride, which is responsible for part of the yellow tint, some yellow organic coloring material, arsenious chloride, and

free chlorine. The acid frequently gives a residue when evaporated, and this must of course represent some impurity. It is sometimes adulterated with calcium chloride, since the price obtained depends upon the specific gravity of the solution, and this may be raised by dissolving calcium chloride in it.

Classification of Chemical Interactions and Exercises Thereon. — So far we have defined ten more or less distinct kinds of chemical change: **Combination** (p. 14), **decomposition** (p. 15), **dissociation** (p. 121), **displacement** (p. 99), **substitution** (p. 176), **double decomposition** (p. 99), **hydrolysis** (p. 181), **oxidation** (pp. 72, 110, 172), **reduction** (pp. 72, 110), and **electrolysis** (p. 19). In one or two of these classes all the actions are **reversible**, in others some are reversible and some are not. Illustrations of every one of these will be found in the present chapter. The classes are not mutually exclusive. Some actions belong to one class or another according to our point of view at the moment. The ability readily to classify each phenomenon, as it comes up, requires precisely that grasp of the framework of the science which the reader must seek speedily to attain. For example, let him classify the following actions: 1. Action of heat on chloroplatinic acid; 2. of potassium on water; 3. of heat on potassium chlorate; 4. of chlorine on metals; 5. of chlorine on turpentine; 6. of chlorine on potassium iodide; 7. of chlorine on methane; 8. of carbon monoxide and chlorine; 9. of sunlight on hypochlorous acid; 10. of sulphuric acid on salt; 11. of zinc oxide and hydrochloric acid; 12. of zinc on hydrochloric acid.

13. Expand the explanation of the tendency of hydrogen chloride to fume in moist air (p. 182).

14. Explain the interaction of steam and iron (p. 110) on mechanical principles similar to those used in describing how hydrogen chloride is formed from salt and sulphuric acid (p. 179).

15. What is the maximum that the temperature of the action (p. 172) of hydrochloric acid on potassium permanganate may attain? Why is this interaction so much more vigorous than that where manganese dioxide is used (p. 173)?

16. In view of the explanations given, can you define the general nature of the "other substances" (p. 172) which may be used to oxidize hydrochloric acid?

Summary of Principles.

It may be useful at this point partially to summarize the principles (general facts) of chemistry so far as they have been developed in the preceding chapters. These principles are given under fourteen heads below. They are stated as far as possible strictly in terms of facts, since hypotheses are not integral parts of chemistry, but are scaffolding temporarily employed to facilitate the erection of the structure of the science. In a later chapter (Chap. xv), some other important principles will be summarized in like manner. To secure more strictly logical arrangement than has seemed advisable in the text, two conceptions which have already been dealt with are held over to the second half of the summary, namely, 17 (valence) and 21 (chemical relations of elements). The reader should give careful thought to the various points, many of which, in a backward view, will be found to have become susceptible of improved statement. We begin the series with the most fundamental fact of all, — the one without which no chemical work would be possible :

1. Each substance has its own set of specific physical properties. By means of these it is recognized and, when necessary, separated from other substances (p. 5).

2. Substances are either simple (elementary), containing only one kind of matter, or compound, containing more than one kind of matter (p. 30).

3. In all chemical phenomena (excepting "internal rearrangements"), changes in the material composition of bodies occur (p. 16).

4. In chemical phenomena there is no change in the total mass of the system (p. 17).

5. Each substance has a definite material composition by weight (p. 41).

6. The proportions by weight in which all chemical combinations take place can be expressed in terms of small integral multiples of fixed numbers, which may be called combining weights, one for each element. That weight of each element which combines with 8 parts of oxygen is called the equivalent weight and has the properties of a combining weight (pp. 48, 50).

7. The proportions by volume in which all chemical interactions involving substances in the gaseous condition take place are expressible by small integers (p. 125).

8. From 6 and 7 it follows that the equivalent weights of all substances occupy, in the gaseous condition and at the same temperature and pressure, volumes which are either equal or stand to one another in the ratio of small integers (p. 126).

9. In every chemical phenomenon a transformation of energy occurs. This results in a redistribution of the chemical energy in the substances concerned, and also in an increase or a decrease in the total chemical energy in the system (p. 26).

Definitions : The word *substance* is applied to a compound of one or more kinds of elementary matter with a certain proportion of chemical energy (p. 32). The word *element* is applied to a variety of simple matter which exists only in combination with energy, and often with other kinds of elementary matter as well (p. 31).

10. In chemical phenomena there is no actual loss or gain, but only transformation of energy (p. 23).

11. Interactions which proceed spontaneously are in general those in which internal energy is transformed into some other variety or varieties of energy (p. 27).

• 12. **Each *substance* has its own set of chemical properties, such as :**

(*a*) **Affinity: the given substance can or can not interact with such and such elementary and compound substances.**

(*b*) Relative activity of the systems in (*a*). This is measured quantitatively by : (α) Relative speed under like conditions (see 13, 14, 18); (β) Relative heat developed, when actions compared can be carried out so that all conditions are alike ; (γ) Relative E.M.F. of cell when the action is so arranged as to give electricity (pp. 28, 76, 111).

13. The speed of every interaction is increased by raising the temperature (p. 72).

14. The speed of interactions is increased or decreased by catalytic agents, each of which is individual in the kind and amount of its effect (p. 74).

CHAPTER XII

MOLECULAR WEIGHTS AND ATOMIC WEIGHTS

AVOGADRO'S hypothesis (p. 131) has proved to be by far the most suggestive and fruitful of all the conceptions of a hypothetical nature in the science of chemistry. We are now in a position to discuss several of its most important applications. To speak in terms of the hypothesis, these concern more particularly the measurement of the relative weights of the molecules of different gaseous substances, and the determination of the most convenient magnitudes for the chemical unit weights (atomic weights; *cf.* p. 50).

Meaning of Avogadro's Hypothesis. — First, we must understand clearly what is implied in the statement that: In equal volumes of all gases, at the same temperature and pressure, there are equal numbers of molecules. It means that, for instance, at 100° and 760 mm., in all specimens of gases the average spacing of the molecules is identical. This condition is independent of the nature of the gas — for example, whether it is a simple or a compound substance, like oxygen and carbon dioxide respectively, or a mixture, like air. It means that when, at some fixed temperature, we fill the same vessel with a number of different gases or gaseous mixtures successively, the number of molecules that it will hold at a pressure, say, of one atmosphere will always be the same. If we take care to keep temperature and pressure the same, the equality in the number of molecules that will enter the jar will take care of itself automatically. In what follows, to avoid continual repetition, it is to be assumed that temperatures and pressures are equal unless the contrary is expressly stated.*

This statement would be *strictly* true only in the case of gases, if such existed, which behaved in ideal accord with the laws of Boyle and Charles. Since, however, in all gases, with the exception of hydrogen, a certain tendency to cohesion between molecules is distinctly noticeable and its amount varies from gas to gas, the density with which the molecules are packed is not *precisely* the same in any two of them. Hence, Avogadro's hypothesis is not perfectly realized in any known

* At the first reading, the beginner is advised to omit the paragraphs set in smaller type, excepting that on pp. 194, 195.

gases. In the case of hydrogen, for example, a divergence from the behavior of an ideal gas exists, but is barely measurable, and in the case of chlorine, it amounts to about 1½ per cent, and is quite conspicuous. This slight irregularity in the packing of the molecules, however, does not interfere with the application of this hypothesis in chemistry.

Two Kinds of Laws in Science. — It will have been observed that the laws of science may be divided into two kinds. Some, like those of conservation of mass and of definite proportions, express the facts with perfect exactness. The divergence between our experimental data and these laws we find to become smaller and smaller the more carefully our experiments are made. The difference between our best determinations and the ideal described by the law, is always less than the known errors of observation. There is, however, a second class of laws in which the opposite is the case. The more carefully our measurements are made, the more clearly is it recognized that the second kind of law does not state the fact with exactness for any single example. The known errors of measurement are in these cases less than the discrepancy between the observed fact and the ideal. The laws of Boyle, of Charles, and of Gay-Lussac are examples of this class. The value of such laws is not impaired by the fact that actual substances are in no case accurately described by them. The law gives us a norm of behavior to which most of the substances conform with a fair degree of closeness. Such a law resembles a limit in mathematics, toward which some expression tends to converge although it does not actually reach it. The first kind of law represents the actual behavior of materials, the second kind of law an average behavior to which no one material adheres with perfect exactness.

Now Avogadro's hypothesis describes in figurative terms some general fact about gases whose exact nature is unknown. Using the molecular hypothesis, we state that this fact has to do with the uniform packing of the molecules in all gases. But, whatever it is, no real gases conform to it with perfect strictness. Avogadro's hypothesis is allied therefore to the second class of laws, to some of which indeed it owes its origin.

The Relative Weights of the Molecules. —According to Avogadro's hypothesis, vessels of equal size filled with different gases contain equal numbers of gaseous molecules. Now equal volumes of different gases differ very markedly in weight, or, in other words, the densities of various known gases cover a wide range of values. Thus, hydrogen is the lightest of all, chlorine is more than thirty-five times, mercuric chloride (corrosive sublimate) vapor over one hundred and thirty-four times as heavy. Since these different weights of equal volumes represent the weights of equal numbers of molecules, the difference must be due to the differing weights of the molecules themselves. The **densities of gases,** therefore, **may be taken as measures of the relative weights of their individual molecules.** The extreme significance of this inference in chemistry will appear as we elaborate upon it.

The various scales on which the densities of gases may be calculated, such as the weights of one liter of each gas, or the weights of volumes equal to that of one gram of air, or of one gram of hydrogen, are illustrated in the first three columns of the following table: *

	Weight of One Liter, 0° and 760 mm.	Density, Air = 1.	Density, Hyd. = 1.	Molecular Weight, Ox. = 32.	Units Composing the Molecule.
Hydrogen . . .	0.090	0.0696	1.00	2.016	$2 \times H = H_2$
Oxygen	1.429	1.105	15.88	32.00	$2 \times O = O_2$
Chlorine . . .	3.166	2.449	35.18	70.90	$2 \times Cl = Cl_2$
Hydrogen chloride,	1.628	1.259	18.09	36.458	$H + Cl = HCl$
Carbon dioxide .	1.965	1.520	21.83	44.00	$C + 2 \times O = CO_2$
Water	0.8045	0.622	8.94	18 016	$2 \times H + O = H_2O$
Mercury . . .	8 932	6.908	99.25	200.0	Hg
Mercuric chloride,	12.097	9.354	134.43	270.90	$Hg + 2 \times Cl = HgCl_2$
Air	1.293	1.00	14.37	28.955	[Mixture]

The values for water (b.-p. 100°), mercury (b.-p. 357°), and mercuric chloride (b.-p. 300°) are measured at high temperatures and reduced by rule (p. 91) to 0° and 760 mm. All the numbers in the first three columns, as they stand, are purely physical in derivation. Those in the second column are obtained from those in the first by using the proportion:

1.293 (wt. 1 l. air) : 1.00 (air = 1) : : wt. of 1 l. any gas : x (dens. of that gas).

To get those in the third column we employ the proportion:

0.090 (wt. 1 l. hyd.) : 1.00 (hyd. = 1) : : wt. of 1 l. any gas : x (dens. of that gas).

The last two columns will be explained presently. Since the numbers in the first column apply to equal volumes (1 l.), and those in the other two stand in constant ratios to them, the weights in each of these two columns represent equal volumes also. In the second, the volume is $\frac{1}{1.293}$ l., and in the third, $\frac{1}{0.09}$ l. The values in any one of the columns represent the relative weights of the molecules of the various substances (see Exercise 1 in this chapter).

* To speak strictly, *the* density of a gas is the weight of 1 c.c. at 0° and 760 mm. Its value for each gas is, therefore, obtained by dividing the numbers in the first column by 1000. The numbers thus obtained are, however, inconveniently small, and, besides, the beginner usually measures the weight of a liter of several gases in the laboratory, and so is more accustomed to the unit employed above.

In order to avoid the creation of unnecessary confusion in the mind of the beginner, the weights of one liter of gas in the above table are, with the exception of that of oxygen, all ideal numbers. They are calculated back from the correct molecular weights made up from the atomic weights. This enables us to show the process by which the molecular weights are derived from the weights of one liter without the exhibition of arithmetical discrepancies which might obscure the principle being explained. The weights of one liter of the various gases, as we have given them, are based on the assumption that the molecules are always packed uniformly in accordance with Avogadro's hypothesis. The actual values are in most cases somewhat different from these, and we attribute the divergencies to the varying degrees of cohesion between the molecules of different substances. Even the weight of one liter of the same gas, after reduction to 0° and 760 mm., is found to vary with the temperature and pressure at which it was examined. This is but natural, since changes in these conditions alter the effects of cohesion. The following table gives the *actual* weights of one liter of the same gases, with a few additional ones, and a comparison will show the extent of the divergencies. The most interesting case perhaps is that of oxygen and hydrogen. The chemical combining weights of these substances are in the ratio of 15.88 : 1.00, while a slight excess of cohesion in oxygen gives the ratio of their densities the value 15.90 : 1.00. These numbers are in both cases based upon Morley's results.

	Weight of One Liter, 0° and 760 mm.	Density, Air = 1.	Density, Hyd. = 1.	Observed Molecular Weight.	Adjusted Molecular Weight.	Units Composing the Molecule.
Hydrogen	0.08987	0.0695	**1.00**	2.012	2.016	$2 \times H = H_2$
Oxygen	1.429	1.105	15.90	**32.00**	**32.00**	$2 \times O = O_2$
Nitrogen	1.251	0.967	13.92	28.00	28.08	$2 \times N = N_2$
Chlorine	3.220	2.490	35.83	72.01	70.90	$2 \times Cl = Cl_2$
Hydrogen chloride	1.641	1.269	18.26	36.69	36.458	$H + Cl = HCl$
Carbon dioxide	1.977	1.529	22.00	44.22	44.00	$C + 2 \times O = CO_2$
Hydrogen sulphide	1.537	1.189	17.10	34.43	34.076	$2 \times H + S = H_2S$
Ammonia	0.772	0.597	8.59	17.29	17.064	$3 \times H + N = NH_3$
Sulphur dioxide	2.927	2.264	32.57	65.55	64.06	$S + 2 \times O = SO_2$
Water	0.8045	0.622	8.95	18.016	18.016	$2 \times H + O = H_2O$
Mercury	8.87	6.86	98.70	198.4	200.0	Hg.
Air	1.293	**1.00**	14.39	28.955	[Mixture]	[Mixture]

The Relation between the Weights of Molecules and the Combining Weights: Atoms.—When we now scrutinize these numbers (p. 192) in the chemical point of view an unexpected complication is disclosed. Using the values in any of the columns, we observe that a molecule of hydrogen chloride actually weighs much less than a mole-

cule of chlorine plus a molecule of hydrogen. In fact, the total weight of the last two molecules (3.256, for example, in the first column) is exactly twice that of the molecule of the compound formed by the union of these substances (1.628). Evidently, to bring the chemical behavior into harmony with the molecular hypothesis, and particularly with Avogadro's hypothesis, on which the assumption that these numbers represent the weights of the molecules is based, one further supposition will have to be made. This is to the effect that the molecule of hydrogen and of chlorine splits into two portions before combination, and the resulting molecule of hydrogen chloride is composed of a half molecule of each.

This conclusion is of importance when we are confronted, as eventually we must be, with the task of harmonizing our combining weights of elements with the weights we assign to molecules. It shows us that our **units of molecular weight** for the above two elements will have to include at least **two chemical unit weights** in order that this splitting may be allowed for, without subdivision of our fundamental combining (atomic) weights. In other words, we may not make 35.18 (column 3) the *molecular* weight of chlorine, and 1 that of hydrogen, for then the molecules of hydrogen chloride would be made up of the half-values, namely, 17.59 of chlorine + 0.5 of hydrogen = 18.09 of hydrogen chloride, and this would involve using 0.5 as the chemical unit of weight for hydrogen. We prefer, therefore, to employ 2 and 70.36 for the molecular weights of hydrogen and chlorine respectively, and 1 and 35.18 for their units of combining weight (later to be renamed atomic weights). Or rather we employ the corresponding slightly larger numbers of the scale Oxygen = 16, which are 2.016 and 70.9 for the molecular weights and 1.008 and 35.45 for the units of combining weight.

The data for water lead to a similar conclusion for oxygen. The proportion by weight of hydrogen and oxygen in water is 2 : 15.88 (p. 125), and this, according to the table (third column), would mean a ratio of two molecules of the former to one of the latter. But the molecule of water weighs only 8.94, or half the sum of these numbers. Hence but half a molecule of free oxygen is required to form a molecule of water. When, therefore, we take 16 for the unit of combining weight in the case of oxygen, the value 32 must be assigned as the weight of the molecule of the free element.

That the molecules of hydrogen, oxygen, and chlorine split when undergoing combination may be shown in another way. Let us represent by small squares

minute volumes of the various gases. The diagram below shows the volume of the hydrogen chloride and that of the two constituents. The two squares side by side represent two volumes of hydrogen chloride containing, say, 100 molecules each, according to this hypothesis. These came from (*cf.* p. 184) one volume of hydrogen containing 100 molecules and one volume of chlorine containing the same number of molecules.

Hydrogen Chloride			Hydrogen		Chlorine
100	100	came from	100	+	100

The 200 molecules of hydrogen chloride must have contained altogether at least 200 fragments of chlorine, since there was a sample of it in each molecule. There were therefore 200 combining units of chlorine, at least. There might of course have been 400 or 600, or even more, since there might be more than one unit of chlorine in each molecule of hydrogen chloride, but there certainly could not have been less than 200. Now the 200 units of chlorine came from a volume containing 100 of the physical subdivisions which this hypothesis postulates. Each of these, therefore, must have contained at least two units. Hence we arrive at the conclusion that the physical particle or molecule of chlorine contains two combining units. We note particularly that this conclusion is due entirely to the fact that we have assumed that there is the same number of molecules in a volume of chlorine that there is in a volume of hydrogen chloride. This conclusion is based therefore upon a certain specific assumption, namely, Avogadro's addition to the molecular hypothesis. At first sight we seem to have sacrificed simplicity by accepting this enlargement of the hypothesis. We shall find, however, that its use greatly simplifies the study of many things in chemistry, and so it is adopted consistently.

To apply the same reasoning to hydrogen, the hydrogen chloride must have contained at least 200 units of hydrogen. These came from one volume of hydrogen gas containing 100 molecules, and there must therefore be two units of hydrogen in each molecule. Regarding this from the other point of view, the 100 molecules of hydrogen have to supply 200 molecules of hydrogen chloride with the element, and must therefore be subdivided in order that this may be accomplished. Hence the molecules of hydrogen cannot be identical with the combining units.

Take now the case of water. Two volumes of water vapor are formed from two volumes of hydrogen and one volume of oxygen. Using the same diagrammatic method, we have two squares representing 100 molecules of water, formed from two squares each containing 100 molecules of hydrogen and one square containing 100 molecules of oxygen.

Water			Hydrogen			Oxygen
100	100	came from	100	100	+	100

Two hundred molecules of water must have contained at least 200 combining units of oxygen. These came from 100 molecules of oxygen, since they came from one volume, and each molecule of oxygen must therefore contain two units.

In the foregoing we have seen that the molecules of chlorine and of hydrogen must be held to contain two units each of the respective

elements. These units are of the same weight as the units of the same elements contained in the molecule of hydrogen chloride. Now, just as the molecule is hypothetically a discrete body, so we may regard its constituent parts as distinct entities. These parts are spoken of as **atoms**, and the word is used so as to be equivalent to our word "units." There is nothing in the facts before us that requires us to suppose that the units or atoms are single particles: they might be clusters of many particles, but they must have definite relative weights, namely, the atomic weights. All that we may infer so far is that, if the atom of hydrogen or of chlorine in a molecule of hydrogen chloride, or the atom of oxygen in a molecule of water, is a cluster of particles, the *molecule* of each of these elements contains twice as many such particles. We shall use the term "atom" sparingly pending fuller explanation in the next chapter.

The Choice of the Value 16 for the Atomic Weight of Oxygen. — When the choice of a final unit of combining weights was under discussion (p. 50), the value 16 was assigned arbitrarily to oxygen in preference to 8, the equivalent weight. The reason for this choice may be found in the preceding sections. If the unit of combining weight had been 8, then 16 would have now to be taken as the molecular weight of the element. But this scale may easily be shown to involve a number less than 1 for the combining unit of hydrogen. For example, the molecule of hydrogen, being only $\frac{1}{15.88}$ as heavy as that of oxygen (p. 192), must receive the value 1.008, and, since this molecule splits in uniting with chlorine and many other elements, the unit of combining weight for hydrogen must be only 0.504 on this scale. Again, and to put the argument differently, the weight of hydrogen chloride occupying the same volume as 16 g. of oxygen is 18.229 g., and in this weight of the compound the amount of hydrogen is only $\frac{1.008}{36.458}$ of the whole, or 0.504 g. Hence, to avoid numbers less than 1, the combining weight of oxygen is raised to 16 (see Exercise 4 in this chapter).

The Chemical Unit of Molecular Weight. — The considerations discussed in the preceding sections enable us to establish a scale of chemical molecular weights for all gaseous and volatile substances. Since O = 16 is our basis of unit or atomic weights, Oxygen = 32 must be the basis of our molecular weights. The molecule of the free element thus contains two units or atoms, and is represented by the formula O_2. The relative weights of the molecules of other substances,

on the new scale, may now be obtained by an arithmetical process similar to those used in converting to the scale Air = 1 and Hydrogen = 1 (p. 192). The results differ from the former ones, however, in possessing a definite relation to chemical facts through the atomic weights, which before was lacking.

In the fourth column of the table (p. 192) the results of this change of scale are given. From the proportion 1.429 : 32.00 : : wt. of 1 l. of a gas : x, we calculate all the values in this column. That is to say, we multiply the weight of one liter of the gas by $\frac{32}{1.429}$. It will be found that perfect harmony between atomic weights and molecular weights has now been secured. Thus the molecule of hydrogen chloride (36.458) is made up of half a molecule or one unit (atom) each of chlorine (35.45) and of hydrogen (1.008). The last column gives the composition of each molecule, the symbols being used in place of the chemical units of weight for which they stand. It will be noted that the molecule of mercury does not split. Hence its molecular and atomic weights are identical, and its formula in the free condition is Hg. Thus all the molecules of elements do not contain two units: each case must be studied separately (see below).

The whole process, condensed in one statement, is as follows: **To obtain the molecular weight of a substance, weigh a known volume of the substance in the state of vapor, reduce the volume by rule to 0° and 760 mm., calculate the weight of one liter by proportion** (this gives the value in the first column), **and convert to the scale oxygen = 32 by multiplying the result by 32/1.429** (for a simpler form of this statement, see below). To record the fact that the gram is the unit of weight employed, the above term may be expanded to the form, **gram-molecular weight.** It is not very appropriate to speak of oxygen = 32 as the *unit* of the system. The real unit is an imaginary gas which has a density one-thirty-second of that of oxygen.

Since the process by which molecular weights are obtained is purely one of calculation from actual measurements, its application involves no use of the molecular hypothesis. At this point, therefore, we emerge from the region of fiction and reach a conception which can be stated in terms of experimental facts alone.

The term gram-molecular weight being somewhat ponderous, we abbreviate it to **molar weight**, and still further to **mole**. Thus, a *mole* of chlorine is 70.9 g. of the element, and a mole of hydrogen chloride is 36.458 g. of the compound. The mole of a substance is the formula weight when molecular formulæ (see below) are employed.

When the above method of calculating the molecular weight from the weight of one liter of a substance is applied to the actual experimental values, the resulting molecular weights necessarily diverge somewhat from the ideal ones which we have given. Thus, since a liter of hydrogen chloride actually weighs 3.221, this number when multiplied by 32 and divided by 1.429 gives the value 72.03. This value of the molecular weight, however, does not contain the atomic weight of chlorine, as found by measuring combining proportions, an even number of times. Consequently, the molecular weights actually determined by experiment have always to be adjusted by a slight numerical change to the nearest value which contains even multiples of the atomic weights of the constituents. In the table on page 193 the observed and the adjusted molecular weights have both been given. The mole is always the adjusted molecular weight and not the observed one.

This process of adjustment does not really involve any uncertainty, because it never requires changes large enough to introduce actual confusion. The adjustment of the observed molecular weight to correspond with the measured combining weights is made in preference to the converse operation because the latter values are always susceptible of exact determination while the former are not. We cannot expect the molecular weights to be accurate, because, in the first place, the measurement of the weight and volume of a gas or vapor is always difficult, and often involves an error of one-half per cent, and, in the second place, the way in which the behavior of gases departs from that of a perfect gas causes the results to vary according to the temperature and pressure chosen for the experiment.

The Chemical Molecule. — The definition of the hypothetical chemical molecule differs slightly from that of a molecule in the general physical sense (p. 129). **Chemical molecules are the units of which *gaseous* bodies are aggregates.** We have means of comparing, roughly, at least, the dimensions of the physical units in gases, liquids, and even solids, and find that in the liquid and solid states the molecules are often multiples of the gaseous ones. The gaseous molecules are, therefore, our standard in chemistry (see, however, Chap. xvii).

It will be seen at once that it would be quite incorrect to define the molecular weight of a substance as the weight of a molecule. We have no definite proof of the existence of molecules as yet, and only the roughest ideas in regard to their weight as individuals. The molecular weight, on the other hand, is a perfectly definite and accurately determined value which would remain in use even if the molecular hypothesis were to be discarded. The conception was first reached, however, through the use of this hypothesis, and hence we might describe a molecular weight as a weight originally fixed by the use of considerations involving molecules.

The Gram-Molecular (Molar) Volume. — The weights in the fourth column of the table (p. 192) must represent equal volumes of

the different gases. This follows from the fact that they are derived from the values in the first column by multiplying by a constant ratio (32/1.429), and the volume in the first column is always 1 liter. The actual dimension of this volume is evidently 32/1.429 liters, which is almost exactly 22.39, or in round numbers **22.4 liters**. This volume at 0° and 760 mm. holds 32 g. of oxygen, 70.9 g. of chlorine, 44.00 g. of carbon dioxide, or, in fact, the molar weight of any gaseous substance. It is called, therefore, the **gram-molecular volume** (G.M.V.) or the **molar volume** (p. 149). It may be defined as **that volume which contains one mole (gram-molecular weight) of any gas at 0° and 760 mm.** At other temperatures and pressures the G.M.V. has correspondingly different values.

The G.M.V. gives us a concrete conception of a molar weight. This volume is represented by a cube (Fig. 69) 28.19 cm. (or about 11.1 inches) high. Like any other volume, it holds the same number of molecules of different gases. Its capacity at 0° and 760 mm. is the number of molecules in 32 g. of oxygen. Hence, in terms of the hypothesis, the weight of any gas which fills it bears to 32 g. the same ratio as the weight of a molecule of that gas to the weight of a molecule of oxygen. We may, therefore, state the **method of finding the molar weight of a substance** more simply than before (p. 197): **Weigh a known volume of the substance, at any temperature and pressure at which it is gaseous, reduce this volume by rule to 0° and 760 mm., and calculate by proportion the weight of 22.4 liters.**

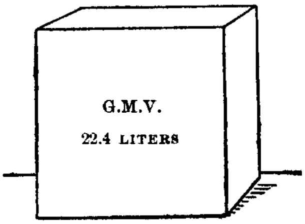


FIG. 69.

It is evident that the chemical molecular weights, adjusted so as to include whole numbers of combining weights, will not all occupy exactly equal volumes. They represent exactly equal numbers of molecules, and the slight differences in the closeness with which the molecules are packed (p. 190) will cause the values of the molar volumes to differ from gas to gas. The values of this volume calculated from the actual weights of one liter of each gas are as follows: Hydrogen, 22.40; oxygen, 22.39; nitrogen, 22.45; chlorine, 22.01; hydrogen chloride, 22.22; carbon dioxide, 22.26; water, 22.39; mercury, 22.55. The average value of this volume in the case of the more nearly perfect gases is 22.4 liters, and this is, therefore, the number which we have used in our definition (see Exercise 3 in this chapter).

Determination of the Atomic Weight of Each Element. — Having learned how the total weight of the molecule is expressed,

using that of oxygen as the standard, we must now return to the combining units of weight. The principle used is that the sum of the units (atoms) represented in the formula of each substance must equal the molecular weight of the latter. Thus we now approach the unit weights from a new standpoint, first ascertaining the molecular weights, and then *dividing the latter between the constituents of the compound.* The following table shows the result of this process for a number of compounds. The molar weights there given are adjusted molecular weights (p. 193), and round numbers are used in some cases.

The method of calculation is as follows: Suppose that we find the molecular weight of phosphorus oxychloride to be 153.35. We then determine by analysis the proportions of the constituents and express them as usual in percentages. The results are, phosphorus, 20.215; chlorine, 69.35; oxygen, 10.435. The problem is to distribute these elements in the same proportion in such a way that the total is equal to the molecular weight. We find the value for phosphorus, for example, by the proportion, 100 : 20.215 : : 153.35 : x, in which we get the value $x = 31$. The proportions of chlorine and oxygen are calculated in the same way, and give the numbers shown in the fourth line of the table.

Substance.	Molar Weight.	Weights of Constituents in Molar Weight.					
		Hydrogen.	Chlorine.	Oxygen.	Phosphorus.	Carbon.	Mercury.
Hydrogen chloride	36.45	1	35.45	. .	. .	. .	. .
Chlorine dioxide	67.45	. .	35.45	32	. .	. .	. .
Phosphorus trichloride	137.35	. .	106.35	. .	31	. .	. .
Phosphorus oxychloride	153.35	. .	106.35	16	31	. .	. .
Phosphoric anhydride	284	. .	. . .	160	124	. .	. .
Phosphine	34	3	. . .	. .	31	. .	. .
Oxygen	32	. .	. . .	32	. .	. .	. .
Ozone	48	. .	. . .	48	. .	. .	. .
Water	18	2	. . .	16	. .	. .	. .
Methane	16	4	. . .	. .	. .	12	. .
Acetylene	26	2	. . .	. .	. .	24	. .
Ethylene	28	4	. . .	. .	. .	24	. .
Formaldehyde	30	2	. . .	16	. .	12	. .
Methyl acetate	74	6	. . .	32	. .	36	. .
Acetic acid	60	4	. . .	32	. .	24	. .
Mercury	200	. .	. . .	. .	. .	. .	200
Mercurous chloride	235.45	. .	35.45	. .	. .	. .	200
Mercuric chloride	270.9	. .	70.9	. .	. .	. .	200

Study of such a table as this, if it were extended to include all known volatile substances, would enable us promptly to pick out the most convenient values for the unit weights of the individual elements. Thus, no compound containing chlorine is known whose total molecular weight contains less than 35.45 parts of this element, although many contain multiples of this amount. Hence this will serve as the unit quantity for describing the proportion in any compound, and will be represented by the symbol Cl. Similarly, 31 is the smallest amount of phosphorus in the table, and is an integral factor of the larger amount. Hence P = 31. For the same reason we choose 12 for carbon, 200 for mercury, and 1 (more exactly 1.008) for hydrogen.

It will now be seen why the equivalents (p. 50) were multiplied by various integers in making the chemical units. The equivalent of carbon was 3. But there is no compound whose molecular weight contains less than 12 parts. Now, for reasons that will appear later, chemists always *adjust the formula* of each volatile substance *so that the total formula-weight* (see below) *is equal to the molar weight.* To accomplish this they multiply, when necessary, all the symbols in the formula by some integer (*e.g.*, N_2O_4). It would thus lead to needless complication to take 3 as the unit amount of carbon, for *every* molecule would then contain four units, or some multiple of four, and every formula C_4 or some multiple of C_4. Having decided that molar weights are to determine the dimensions of the total formula-weight of every compound, we choose the largest units of combining weight that we can, in order that all the chemical transactions of each element may be formulated by means of the smallest possible numbers of units.

The mode of derivation makes all the quantities of any one element in the above table integral multiples of the smallest. Of course, an element might be found of which no volatile compound containing the unit weight was yet known. If methane and formaldehyde were still undiscovered, and only the other four compounds containing carbon were available, we should then take the greatest common measure of 24 and 36, namely, 12, as the unit.

The chemical unit weight or atomic weight of an element may thus be defined as: The **G.C.M.** (greatest common measure) **of the weights of that element found in the molar weights of all its volatile compounds** so far as these have been examined. **It is always a multiple of the equivalent by unity or some other small integer.**

This definition is simply a description of the experimental method of determining atomic weights. The same thing may be expressed in several other ways.

For example, we may say that the atomic weight is the smallest weight of the element found in the molar weight of any of its volatile compounds. This, however, is a less satisfactory definition, because it fails to cover the possibility of no compound containing a single unit (atom) being known.

We may also define the atomic weight of any element as the largest even multiple of the equivalent which can be contained in the molecular weights of all the volatile compounds of the element. That the atomic weight, determined by the above method, must necessarily be a multiple of the equivalent weight, hardly requires demonstration. In compounds containing oxygen, Gay-Lussac's law shows that the quantity of oxygen in the molecular weight of the compound must be an even multiple or sub-multiple of 32 and therefore an even multiple of 8. Hence the weight of the other constituent combined with this amount of oxygen must be an even multiple of the quantity which would combine with 8 parts of oxygen. That is to say, it must be the combining weight, or an even multiple of it. If the compound does not contain oxygen, then, according to Gay-Lussac's law, the volumes of the compound and of oxygen which would interact must stand to one another in the ratio of two integers. From this fact, by similar reasoning, we reach the same conclusion as before.

The application of the criterion which Avogadro's hypothesis furnishes for the determination of chemical unit weights was neglected for many years. Although it was first suggested by Avogadro in 1811, and almost immediately afterwards, independently, by Ampère, it was not until Cannizzaro, still professor of chemistry in Rome, recalled attention to its usefulness in 1858, that the values to which it led began finally to be adopted by chemists. Consequently, during the first half of the nineteenth century, through the absence of any definite standard for chemical unit weights, much confusion existed. This was not remedied very promptly, even after 1858, for the unit weights based upon Avogadro's principle were not accepted by all chemists simultaneously. Thus, when $O = 8$, the formula of water is HO, and this mode of writing its composition will be found in many chemical works published during the first two-thirds of the nineteenth century.

There is one feature of the definition to which attention must be drawn specifically. The atomic weight, according to the definition, is chosen from amongst the values given by known volatile compounds. When these are few in number, there is always a possibility that the actual minimum has not been found amongst them. There are, however, as we shall see, other independent ways of fixing the values of the atomic weights, and we have now good reason to believe that few of those at present in use will require to be altered in consequence of future discoveries.

The Accepted Atomic Weights of the Elements. — The most trustworthy measurements have been selected in making up the following list of unit weights. It is the one approved by an international committee (1906) consisting of F. W. Clarke, T. E. Thorpe, Karl Seubert, and Henri Moissan.

NAME OF ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	ELEMENTARY SUBSTANCE FIRST ISOLATED BY:	DATE.*
Aluminium	Al	27.1	Wöhler	1827
Antimony (Stibium)	Sb	120.2	Basil Valentine	15th Cent.
Argon	A	39.9	Rayleigh and Ramsay	1894
Arsenic	As	75.0	Albertus Magnus	13th Cent.
Barium	Ba	137.4	Davy	1808
Bismuth	Bi	208.5	Ment. by Basil Valentine	15th Cent.
Boron	B	11.0	Gay-Lussac and Thénard	1808
Bromine	Br	79.96	Balard	1826
Cadmium	Cd	112.4	Stromeyer	1817
Caesium	Cs	132.9	Bunsen and Kirchhoff	1861
Calcium	Ca	40.1	Davy	1808
Carbon	C	12.00	. . . .	Prehistoric
Cerium	Ce	140.25	Mosander	1839
Chlorine	Cl	35.45	Scheele	1774
Chromium	Cr	52.1	Vauquelin	1797
Cobalt	Co	59.0	Brand	1735
Columbium (Niobium)	Cb	94	Hatchett	1801
Copper (Cuprum)	Cu	63.6	. . . .	Prehistoric
Erbium	E	166	Mosander	1843
Fluorine	F	19	Moissan	1886
Gallium	Ga	70	Lecoq de Boisbaudran	1875
Germanium	Ge	72.5	Winkler	1886
Glucinum (Beryllium)	Gl	9.1	Wöhler and Bussy	1828
Gold (Aurum)	Au	197.2	. . . .	Prehistoric
Helium	He	4	Ramsay and Cleve	1895
Hydrogen	H	1.008	Cavendish	1766
Indium	In	115	Reich and Richter	1863
Iodine	I	126.97	Courtois	1811
Iridium	Ir	193.0	Smithson Tennant	1804
Iron (Ferrum)	Fe	55.9	. . . .	Prehistoric
Krypton	Kr	81.8	Ramsay and Travers	1898
Lanthanum	La	138.9	Mosander	1839
Lead (Plumbum)	Pb	206.9	Mentioned by Pliny	Prehistoric
Lithium	Li	7.03	Arfvedson	1817
Magnesium	Mg	24.36	Liebig and Bussy	1830
Manganese	Mn	55.0	Gahn	1774
Mercury (Hydrargyrum)	Hg	200.0	First ment. by Theophrastus	300 B.C.
Molybdenum	Mo	96.0	Hjelm	1790
Neodymium	Nd	143.6	Auer von Welsbach	1885
Neon	Ne	20	Ramsay and Travers	1898
Nickel	Ni	58.07	Cronstedt	1751
Nitrogen	N	14.04	Rutherford	1772
Osmium	Os	191	Smithson Tennant	1804
Oxygen	O	16.00	Priestley	1774
Palladium	Pd	106.5	Wollaston	1803
Phosphorus	P	31.0	Brand	1674
Platinum	Pt	194.8	. . . .	16th Cent.
Potassium (Kalium)	K	39.15	Davy	1807

* In cases where the elementary substance has not been isolated, the date of admission to the list of elements is given.

Name of Element.	Symbol.	Atomic Weight.	Elementary Substance First Isolated by:	Date.*
Praseodymium	Pr	140.5	Auer von Welsbach	1885
Radium	Ra	225	Curie	1902
Rhodium	Rh	103.0	Wollaston	1803
Rubidium	Rb	85.5	Bunsen and Kirchhoff	1861
Ruthenium	Ru	101.7	Claus	1845
Samarium	Sa	150.3	Lecoq de Boisbaudran	1879
Scandium	Sc	44.1	Nilson and Cleve	1879
Selenium	Se	79.2	Berzelius	1817
Silicon	Si	28.4	Berzelius	1823
Silver (Argentum)	Ag	107.93	. . . .	Prehistoric
Sodium (Natrium)	Na	23 05	Davy	1807
Strontium	Sr	87.6	Davy	1808
Sulphur	S	32.06	. . . .	Prehistoric
Tantalum	Ta	183	Eckeberg	1802
Tellurium	Te	127.6	Müller von Reichenstein	1782
Thallium	Tl	204.1	Crookes	1861
Thorium	Th	232.5	Berzelius	1828
Tin (Stannum)	Sn	119.0	. . . .	Prehistoric
Titanium	Ti	48.1	Gregor	1789
Tungsten (Wolfram)	W	184	Bros. d' Elhujar	1783
Uranium	U	238.5	Peligot	1841
Vanadium	V	51.2	Berzelius	1831
Xenon	X	128	Ramsay and Travers	1898
Ytterbium	Yb	173.0	Marignac	1878
Yttrium	Yt	89.0	Wöhler	1828
Zinc	Zn	65.4	Ment. by Basil Valentine	15th Cent.
Zirconium	Zr	90.6	Berzelius	1825

Molecular Formulæ of Compounds. — Since we have all along been using the symbols to represent the atomic weights of the elements, no change in this respect will be required.

The formulæ of compounds are used to express the proportion by weight of the constituent elements. To this must now be added the condition that the total formula-weight must be made up so as to equal the molecular weight, in all cases where the latter is known. Thus, in acetylene (p. 200) the proportion of carbon to hydrogen, expressed in the simplest terms, is 12 : 1 (= CH). But the molecular weight is 26, hence the formula must be C_2H_2. Similarly in ethylene the expression CH_2 would correctly represent the proportion by weight of the constituents, but not the molecular weight. The latter compels us to use C_2H_4 as the formula. In like manner acetic acid is

* In cases where the elementary substance has not been isolated, the date of admission to the list of elements is given.

$C_2H_4O_2$ and not CH_2O. Here the usage is justified by the fact that, although the composition of acetic acid is the same as that of formaldehyde (CH_2O), the materials themselves are entirely different. The **molecular formulæ** $C_2H_4O_2$ and CH_2O show that they are different (see Exercise 2 in this chapter).

Molecular Formulæ of Simple Substances. — Hydrogen *in the free condition* has two chemical units in its molecule (p. 194), and hence its molecular formula is H_2. In other words, two unit weights (atoms) of the *element* (*cf.* p. 32) combine with each other to form the free *substance*. In combination with *other* elements, as in PH_3, HCl, C_2H_4, and H_2O, any number of unit weights of hydrogen may be used. Similarly the molecular formula of free chlorine is Cl_2, since its molecular weight is 70.9. On the other hand, that of mercury is Hg, for 200 (p. 200) is at once its unit of combining weight and its molecular weight. The molecules of many other elements, such as cadmium, zinc, potassium, and sodium, contain but one chemical unit (atom).

On the other hand, phosphorus vapor has the molecular formula P_4 and sulphur vapor S_8, although in these cases measurements at higher temperatures give smaller values. Thus at 1700° the molecular weight of phosphorus is 91, showing it to be composed partly of molecules of the formula P_2. Sulphur vapor at 800 becomes wholly S_2. When the temperature is lowered, S_8 is re-formed. Iodine (*q.v.*) supplies the most interesting example of this kind.

The molecular weight of many of the elements is by no means a fixed quantity. Its value often depends, as the above examples show, upon the temperature at which it is measured. Thus, while the molecular weight of oxygen does not vary to any appreciable extent between its boiling-point (– 182.5°) and 1700°, many of the other elements show very marked changes. This seems to indicate that while there is only *one* stable molecular form of the substance oxygen, there are *several* molecular arrangements of some of the elements which have at least a certain degree of stability. While the data in regard to many of these cases are given under their respective elements, it may be worth while to collect them together in this place in order to show between what limits the variations occur. An examination of the following table exhibits the fact that, for example, bromine is all Br_2 up to 750°, but beyond this there is a small but measurable amount of dissociation. Again, iodine is all I_2 up to 448°. Beyond this temperature the density diminishes, and when 1700° has been reached the molecules have all been completely dissociated. Phosphorus, even at 1700°, is only partially decomposed into molecules of the formula P_2, while arsenic at the same temperature is almost completely As_2.

Molecular Weights of the Elements at Various Temperatures.

ELEMENT.	TEMP.	OBSERVED MOL. WT.	NEAREST MULTIPLE OF ATOMIC WEIGHT.	REMARKS.
Antimony. . .	1640°	283	Sb_2 = 240.4	Some Sb_4
Arsenic . . .	644°	308.4	As_4 = 300	All As_4
Arsenic . . .	1700°	159.0	As_2 = 150	All As_2
Bismuth . . .	1640°	293.0	Bi_2 = 417.0	Much Bi
Bromine . . .	750°	160	Br_2 = 159.9	All Br_2
Bromine . . .	1050°	150.5	Br_2 = 159.9	Slight dissociation
Cadmium. . .	1040°	114	Cd = 112	All Cd
Iodine. . . .	448°	254.8	I_2 = 253.94	All I_2
Iodine. . . .	1700°	127	I = 126.97	Complete dissociation (I)
Mercury . . .	448°	198.5	Hg = 200	All Hg
Mercury . . .	1730°	198	Hg = 200	Still Hg
Oxygen . . .	1700°	32	O_2 = 32	All O_2
Phosphorus . .	313°	128	P_4 = 124	All P_4
Phosphorus . .	1700°	91.2	P_4 = 124	Much P_2
Potassium . .	Red heat	37.6	K = 39.15	All K
Selenium . . .	860°	222	Se_2 = 158.4	. . . .
Selenium . . .	1420°	164.4	Se_2 = 158.4	Nearly all Se_2
Sodium . . .	Red heat	25.4	Na = 23.05	All Na
Sulphur . . .	193°	251	S_8 = 256.5	(2.1 mm. press.)
Sulphur . . .	800°	64.2	S_2 = 64.1	All S_2
Sulphur . . .	1719°	63.6	S_2 = 64.1	Still S_2
Tellurium . .	1400°	260	Te_2 = 255.2	. . . .
Thallium . . .	1730°	412.4	Tl_2 = 408.2	All Tl_2
Zinc	1740°	76.4	Zn = 65.4	All Zn

The case of oxygen demonstrates clearly the necessity of using molecular formulæ, even for simple substances. The table of analyzed molecular weights (p. 200) shows two substances containing nothing but oxygen. Ozone (*q.v.*) has a molecular weight 48, being a gas exactly one-half heavier than ordinary oxygen. Its formula, therefore, is O_3, while that of oxygen is O_2. Oxygen and ozone are entirely different chemical individuals. The latter has, for example, much greater activity, as is shown by the fact that silver rusts when exposed to it.

The molecular constitution of the familiar gases, like hydrogen and chlorine, suggests one reason for the fact that they do not unite at once when mixed. If they were made up of free chemical units, it is difficult to see how these could continually encounter one another as they moved about, without combining. But the molecular formulæ suggest that each gas is really in combination already (with itself), and hence is indifferent to the presence of the other. Indeed, the fact

that hydrogen shows no evidence of dissociation into atoms when heated, since its molecular weight is the same at all temperatures, proves it to be a very stable combination. Both water and hydrogen chloride show distinct signs of decomposition when treated in the same way. When a mixture of hydrogen and chlorine is heated so as to dissociate a few of the molecules, the union of the elements cross-wise begins at once, and the heat developed by this union quickly carries the action through the whole mass. Of course this explanation is based upon our hypothesis and, as such, is of the same imaginary description as everything connected with that hypothesis. It cannot be verified by experiment.

While the use of the molecular hypothesis, in explaining the constitution of elements like hydrogen and chlorine, and their indifference to one another when mixed, is probably the most easy for the beginner to understand, it is not the safest in the scientific point of view. It is preferable to employ the conception of energy and to say that when the mixture is heated locally, the amount of energy in the parts of the components which are affected is increased, and consequently their chemical activity is raised. When the energy which they contain reaches a certain potential, the chemical change begins.

To prevent misconception, it must be repeated that these formulæ, O_2 and O_3, apply only to the forms of *free* oxygen, and at present these are the only forms of the simple substance which are known with certainty. In combination, any number of units of the element may be contained in a composite molecule. Thus we have H_2O, CO_2, HNO_3, $H_2C_2O_4$, $C_6H_{12}O_6$ (grape sugar), and so forth, without limit.

Attention must be called specifically to the fact that the chemical unit of combining weight for an element can *not* be determined by measuring the molecular weight of the *simple substance*. We have no means of knowing how many units are contained in the molecule until the unit itself shall have been fixed. This is done by comparison of the molecular weights of several *compounds* of the element with the results of analysis of those compounds (p. 200).

Dissociation of Compounds. — Dissociation of the kind undergone by sulphur vapor and by iodine vapor (p. 205) is not confined to simple substances. Phosphorus pentachloride can be converted into vapor without much difficulty. Its molecular weight, if it underwent no chemical change during the volatilization, would be 208.25. The density actually observed at 300° gives by calculation not much more than half this value. The explanation is found when we examine the

nature of the vapor more closely. We find that it is a mixture of phosphorus trichloride and free chlorine, resulting from a chemical change according to the equation: $PCl_5 \rightleftarrows PCl_3 + Cl_2$. The low value of the density tells us at once that dissociation has taken place. *From the value of the density at various temperatures*, we may even calculate the proportion of the whole material which is dissociated. At 300° it is 97 per cent; at 250°, 80 per cent; and at 200°, 48.5 per cent (see Exercise 10 in this chapter).

Chemical Interactions Studied by Observation of Volumes: Molecular Equations. — According to Avogadro's hypothesis, if we filled a succession of vessels of equal dimensions with different gases, and could arrest the motion of the particles and observe their disposition, we should find that the average distance from particle to particle would be the same in all cases. This would be true whether our vessels were filled with single gases, with homogeneous mixtures, or with gases in layers. Such being the case, if any chemical change is brought about in the mass which results in a multiplication of the molecules, it is evident that the volume will have to increase in order that the spacing may remain the same as before. If any chemical action results in a diminution of the number of molecules, then a shrinkage must take place in order that the spacing may be preserved as before. Thus in a mixture of hydrogen and chlorine, according to our hypothesis, neighboring molecules of hydrogen and chlorine simply exchange units, so that $H-H + Cl-Cl$ becomes $H-Cl + Cl-H$. There being no alteration in the number of particles, no change in volume occurs. In the case of water, on the other hand,

$$H-H + O-O + H-H \text{ becomes } H-O-H + H-O-H.$$

Since the oxygen molecules, which form a third of the whole, disappear into the molecules of hydrogen, the tendency to preserve spacing results in a diminution of the volume by one-third (p. 126).

This method of looking upon chemical interactions between gases gives us the nearest sight which we can have of the behavior of the molecules themselves. We cannot observe the individual molecules, but in consequence of the spatial arrangement which we suppose them to observe, the outward change in the volume of a large aggregate of molecules enables us to draw conclusions at once in regard to the behavior of the single molecules in detail.

Take, for example, the case of the burning of solid sulphur in oxygen gas within a closed space. We find that the volume of the gas does not alter during the process. It takes up the sulphur into itself. The fact that no alteration in volume occurs, leads us to infer that there are no more gaseous molecules after the action than before it. A molecule of oxygen contains two units, so that the molecule of the product must also contain two units of oxygen, with sulphur in addition. This harmonizes with the formula employed for the substance which, as we have seen, is SO_2.

Now, by using in our equations the molecular formulæ for all gaseous substances, we gain the advantage of having a record of the changes in volume as well as of the proportions by weight. Thus, if we write $S + 2O \rightarrow SO_2$, the equation shows the proportions by weight correctly. But the equation

$$S + O_2 \rightarrow SO_2$$

records, in addition, the fact that the number of molecules of oxygen and of sulphur dioxide is the same. These being the only gases, there is therefore no change in volume. Again, if we write $H + Cl \rightarrow HCl$, the proportions by weight are correct. But it appears as if two gaseous particles had given one, and that therefore the volume should have been reduced to one-half, which is not the case. The **molecular equation,**

$$H_2 + Cl_2 \rightarrow 2HCl,$$

shows the same relative weights of material, together with the additional fact that there are equal numbers of molecules of the two ingredients, and as many molecules in the product as there are in both ingredients together. In such an equation each formula of a gaseous substance represents one volume. The most instructive chemical equations are thus the molecular ones, and *they will be used exclusively in the sequel* (see Atomic hypothesis).

When we know the molecular formulæ of the single substances concerned in an action, the equation can be made and the change in volume determined without actual measurement. For example: What volume change will be observed when a mixture of carbon monoxide and oxygen has exploded, and the temperature has once more reached that of the room? The molecular formulæ are CO, O_2, and CO_2. The equation representing the weights is $CO + O \rightarrow CO_2$. The molecule of

oxygen, however, being O_2, we cannot employ less than this quantity in a molecular equation, so that the equation becomes:

$$2CO + O_2 \rightarrow 2CO_2.$$

Three molecules, therefore, give two, throughout the whole mass, and therefore three volumes will become two if the pressure and temperature are the same at the beginning and end of the action.

If we remember that all volatile compounds of carbon and hydrogen burn to form water and carbon dioxide, the molecular equation for any such combustion may easily be made, and the volumes of all the materials ascertained. The volumes of solids and liquids are always insignificant. Hence, if water is a product, only its volume as steam is given by the equation (see Exercises 2 and 5–9 in this chapter).

The molecular formula of acetylene is C_2H_2. When this gas is mixed with oxygen in sufficient amount, a violently explosive mixture is obtained. The chemical action results in the formation of carbon dioxide and water. The equation $C_2H_2 + 5O \rightarrow 2CO_2 + H_2O$ represents the change so far as the weights of material are concerned. But we must use nothing but complete molecules if we wish to learn the volume relations. To secure the oxygen in multiples of two combining weights, we must double the whole equation, when it appears in the form:

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O.$$

We then see that seven molecules become six, so that the change in volume, above 100°, will be in the same proportion. Below 100° the water condenses, and the carbon dioxide is the only gas produced.

Other Methods of Determining Molecular Weights. — The method we have described is necessarily restricted in its application to volatile substances which are not decomposed when converted into vapor. The similarity between the dissolved and the gaseous states (*cf.* p. 150), however, opens up a much wider field for the use of what is essentially the same method. Subject to certain exceptions, equal volumes of solutions having the same temperature and osmotic pressure contain equal numbers of molecules. Hence all the reasoning we have applied to gases may be used *mutatis mutandis* in connection with solutions (see Chap. xvii).

Properties Possessed by Atomic Weights, but not by Equivalents. — It is manifest that equivalents are much simpler in nature and much more easily ascertained than atomic weights. It will be expected, therefore, that we shall be able to show that the units Na = 23, Cu = 63.6, Al = 27.1, C = 12, etc., give a better view of the relations of the elements than do the equivalents 23, 31.8, 9.03, and 3 respectively. Now, these unit (atomic) weights are found to have five

important properties, at least,* which would disappear from view entirely if equivalents were employed. This gain may be set against one general law appertaining to equivalents which would be sacrificed if we were to use atomic weights exclusively. Hence our distinct preference for the atomic weights, as well as our retention of the equivalents for certain purposes.

The first great property of atomic weights is that they are in close correspondence with the volume relations in chemical change, which the equivalents are not. This matter has formed the main subject of the present chapter. The atomic weight of an element can have but one value and is definitely determinable. The equivalent may have more than one value, because an element, if it gives several series of compounds (p. 105), will have as many different equivalents.

The other three properties of atomic weights concern: Dulong and Petit's law, the periodic system, and the conception of molecular structure. The property of equivalents which is not possessed by the unit weights is described by Faraday's law (*q.v.*).

Dulong and Petit's Law. — It was first pointed out (1818) by Dulong and Petit, of the École Polytechnique in Paris, that when the atomic weights of the elements were multiplied by the specific heats of the simple substances in the solid condition, the products were approximately the same in all cases. In other words, the specific heats are inversely proportional to the magnitudes of the atomic weights. The table, in which round numbers have been used for the atomic weights, shows that the product lies usually between 6 and 7, averaging about 6.4:

Element.	Atomic Wt.	Sp. Ht.	Product.	Element.	Atomic Wt.	Sp. Ht.	Product.
Lithium	7	.94	6.6	Iron	56	.112	6.3
Sodium	23	.29	6.7	Zinc	65.4	.093	6.1
Magnesium	24.4	.245	6.0	Bromine (Solid)	80	.084	6.7
Silicon	28.4	.16	4.5	Gold	197	.032	6.3
Phosphorus (Yellow)	31	.19	5.9	Mercury (Solid)	200	.0335	6.7
Calcium	40	.170	6.8	Uranium	238.5	.0276	6.6

* A sixth is mentioned in Chap. xvii, section on the ionic hypothesis.

The conspicuous exceptions occur among the elements with low atomic weights only. The products for four of these, the atomic weights being given in parentheses, are as follows: Glucinum (9), 3.7, boron (11), 2.8, carbon (12), 1.7, and silicon (28.4), 4.5. Further investigation shows, however, that in the case of precisely these elements the value found for the specific heat varies very markedly with the temperature at which the specific heat is measured. Their specific heats become rapidly greater the higher the temperature. Thus at 985° the specific heat of the diamond (carbon) is 0.45, which when multiplied by the atomic weight gives the product 5.5. So that even the exceptional elements tend to come into line when the specific heat is measured at higher temperatures — and Dulong and Petit's statement does not limit our choice to any one temperature.

Another way of expressing this law will give it greater chemical significance. The specific heats are the amounts of heat required to raise equal weights of the various elements through one degree. Now these *equal weights* contain fewer chemical units in proportion as the chemical unit weight is greater. Hence this law may be put in the form: Less heat is required to raise the temperature of equal weights in proportion as the number of chemical units they contain is smaller. In fact, equal numbers of units require equal amounts of heat to raise them through equal intervals of temperature. In other words, **atomic weights of all elements have equal capacities for heat.**

This being true, the equivalents, if used instead of the atomic weights, must give widely varying products. The quantities of heat required to raise equivalent weights through one degree are either equal to, or are fractions of, those required for the atomic weights, according to the valence of the element. Hence the law applies only to atomic weights, and not to equivalents.

It will be seen at once that although the law of Dulong and Petit is purely empirical, it may nevertheless be used for fixing the atomic weight of an element of which no volatile compounds are known. We can always measure the equivalent with considerable exactness, and, when this has been multiplied by the specific heat of the free substance, we can see at a glance what integral factor will raise the product to the neighborhood of 6.4. For example, analysis shows us that in calcium chloride the proportion of chlorine to calcium, using the known atomic weight of chlorine as one term of the proportion, is 35.5 : 20. If calcium is univalent, 20 is its atomic weight. If it is bivalent, two units of chlorine are combined with 40 parts of calcium, and 40 is its atomic weight. If it is trivalent, three units of chlorine are united with 60 parts of calcium, etc. All we learn in reference to the atomic weight of calcium from this analysis is that its value

is 20 or some integral multiple of 20. Nor can we fix the upper limit, for we are unable to obtain the weight of a known volume of calcium chloride vapor and so determine the molecular weight. But the specific heat of calcium being 0.170, we multiply this number by 20, and get the product 3.4. This is only half large enough, so we assume that 40 is a more probable value for the atomic weight of calcium. The product is then 6.8, which agrees fairly well with the average for other elements. We decide, therefore, that the symbol Ca shall represent forty parts by weight. The formula of calcium chloride is therefore $CaCl_2$, and calcium is bivalent.

It will be seen that this does not supply us with a method of ascertaining chemical unit weights independently of any chemical experiment. We cannot measure the specific heat and use the quotient from division of this number into 6.4, for we do not know in advance that the product for the element will have exactly this value. It may be below 6, or it may be as high as 7. In the case of calcium, for example, $6.4 \div 0.17 = 37.65$. Now 37.65 is 5 per cent below the real value of the chemical unit, and even the roughest measurement of a chemical combining weight need never be more than 1 per cent in error. Hence the atomic weight must be founded upon the determination of the equivalent, which can be measured with accuracy. The rule discussed in this section can be used only to ascertain what multiple of the equivalent shall be accepted as the atomic weight after the equivalent itself has been measured with care. In other words, this is a method of adjusting the result of chemical experimentation, and cannot supersede it altogether.

Periodic System: Molecular Structure. — The periodic system (*q.v.*) is an arrangement of the elements in the order of magnitude of their *atomic weights*. The elements when placed in this order are found to be grouped in a highly remarkable manner according to chemical likeness. An arrangement in the order of the equivalents leads to no significant grouping at all.

The conception of molecular structure finds its chief application in the chemistry of the compounds of carbon, and a description of its most remarkable services to chemistry would involve discussions far too elaborate to be included in this volume. The graphic formulæ (*q.v.*) which represent this structure find little application in inorganic chemistry. A simple illustration only can be given.

If the symbol *C* stood for three parts (the equivalent) of carbon, methane would receive the formula *C*H, the proportion of its constituents by weight being 3 of carbon and 1 of hydrogen. But, when we mix this gas with chlorine and expose the mixture to sunlight, no less than four different compounds are produced (*cf.* p. 176). With C = 3,

their formulæ would be C_4H_8Cl, C_2HCl, C_4HCl_3, and CCl, the carbon being univalent. The relations of these substances are much simplified when we change to molecular formulæ and substitute $C = 12$ for $C_4 = 12$, making the carbon quadrivalent. We then perceive that we are displacing successively the four hydrogen units in one molecule, and that the substances are CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. The whole prodigious growth of the chemistry of the compounds of carbon, which has taken place during the last half century, has been the result of the employment of this seemingly slight improvement by Kekulé and Couper, independently of one another, in 1858.

Thus, quite aside from the molecular hypothesis and Avogadro's addition to it, we have now found ample independent justification for the multiplication of the equivalents by integers and for the conception of valence which results from this. Indeed, if Avogadro's hypothesis had not suggested this multiplication, it would have come about eventually even in the absence of any molecular hypothesis. Dulong and Petit's law would have been sufficient alone to direct attention to the atomic weights, and their other properties could not long have escaped discovery.

The existence of the law of Dulong and Petit and the periodic law, together with the services of structural formulæ to organic chemistry, all demonstrate that atomic weights are of vastly greater significance in the science than are equivalent weights. And there are other immense ranges of facts aside from those covered by these conceptions, which are all dependent upon the atomic weights. That almost the whole systematization that has been secured in chemistry should thus center in this one point, furnishes the strongest circumstantial evidence that Avogadro's hypothesis represents very closely some fundamental property of all gases. This independent inductive evidence in favor of Avogadro's principle is especially worth noting because the deduction of the principle from the data of the kinetic-molecular hypothesis is not absolutely rigid. It involves certain assumptions which, while they are plausible enough, are still assumptions.

Application to the Case of a New Element. — By way of reviewing the principles explained in the chapter, let us apply them to the imaginary case of a newly discovered element. The bromide of the element is found to be easy of preparation and to be volatile. It contains 30 per cent of the element, and its vapor density referred to air is 11.84.

To find the equivalent of the element, that is, the amount combined with 80 parts (the equivalent) of bromine, we have the proportion $70 : 30 :: 80 : x$, from which $x = 34.3$. The atomic weight must be this, or some small multiple of it.

The G.M.V. of air weighs 28.955 g. (p. 192). Hence the same volume of the vapor of this bromide, which is 11.84 times as heavy as air, will weigh 28.955×11.84, or 342.84 g. This is therefore the molar weight of the compound.

Now 30 per cent of this is the new element. $342.84 \times 30 \div 100 = 102.85$. So long as no other volatile compound is known, we adopt this as the atomic weight. The rest of the molar weight (240 parts) is bromine. Thus the formula of the compound is $ElBr_3$, and from this we see that the element is trivalent.

In case no volatile compound of the element can be formed, some of the free simple substance is made, say by electrolysis, and its specific heat is determined. Application of Dulong and Petit's law then gives the multiple of the equivalent that constitutes the atomic weight.

Exercises. — 1. The weight of 1 l. of a gas at 0° and 760 mm. is 5.236 g. What is the density referred to air and to hydrogen, and what is the molecular weight (pp. 192, 199)?

2. The molecular weight of cyanogen is 52.08. It contains 46.08 per cent carbon and 53.92 per cent nitrogen. What is its density referred to air, and what the weight of 1 l. at 0° and 760 mm.? What is the formula of the substance (p. 204)? Exploded with oxygen it forms carbon dioxide and free nitrogen. What will be the relative volumes of the materials before and after the interaction (p. 210)?

3. The density (referred to air) of sulphur trioxide vapor, as measured at a certain temperature and pressure, was 2.85. What is the observed molecular weight? What is the actual G.M.V. in this case, and why does it differ from the average value (p. 199)?

4. If the atomic weight of oxygen were taken as 100, what would be the atomic weight of hydrogen?

5. Knowing the molecular formulæ of gaseous substances, it is unnecessary to burden our minds with other data in regard to their relative weights. Is hydrogen chloride (HCl) heavier or lighter than carbon dioxide (CO_2)? A G.M.V. of the former weighs $H + Cl = 36.45$ g., and of the latter $C + 2O = 44$ g. (p. 204). Hence the former is a little lighter. Remembering that the G.M.V. of air weighs 28.955 g., we can compare the weight of any gas with that of air in the same way.

What are the relative weights of acetylene and sulphur dioxide as compared with air?

6. Our equations hitherto have attempted to show only the numbers

of units in various actions. In future nothing but molecular formulæ of free elements must be used (p. 209). For example (p. 59), $2HgO \rightarrow 2Hg + O_2$. Write in molecular form all the equations involving gases which are found in the preceding chapters.

7. Work out the molecular formulæ of all the substances in the table of analyzed molecular weights (p. 200).

8. If the problem is to know what volume of a gas is produced from, or combines with, a certain weight of some substance, the use of the G.M.V. leads us most directly to the answer. Thus, what volume of oxygen is obtainable from 60 g. of potassium chlorate? First, we write the molecular equation, that is, the equation showing nothing but complete molecules of all gases concerned:

$$\begin{array}{ccccc} 2KClO_3 & \rightarrow & 2KCl & + & 3O_2, \\ 2 \times 122.5 & & 2 \times 74.5 & & 3 \times 32, \end{array}$$

and place below each formula the weight of material it represents. Now 32 g. of oxygen occupy 1 G.M.V. or 22.4 liters. Hence 245 g. of potassium chlorate give 3×22.4 liters, and therefore 60 g. give $60 \times 3 \times 22.4 \div 245$ liters of oxygen at 0° and 760 mm. If a different temperature and pressure is to be considered, either the G.M.V. or the answer must be converted by rule to the given conditions.

What volume of oxygen at 10° and 750 mm. is obtainable by heating 50 g. of barium peroxide?

What volume of oxygen at 20° and 760 mm. is required to convert 16 g. of iron into rust (Fe_2O_3)?

9. Write out the molecular equations for the union of alcohol vapor (C_2H_6O) and oxygen (p. 210); for the interactions of methane and chlorine (pp. 176, 214); and for the burning of phosphorus (vapor) in oxygen. Deduce the volume relations of the initial substances and of the products at various temperatures in each case.

10. At 1700° the average molecular weight of phosphorus is 91 (p. 206). What percentage of molecules of P_4 has been dissociated into P_2?

11. Show that, if an element has more than one equivalent weight, the atomic weight must be some multiple of each of the equivalents by a whole number.

12. Prove, without the use of anything hypothetical, that 16 is preferable to 8 for the atomic weight of oxygen, because the smaller number involves a fractional value for the atomic weight of hydrogen.

CHAPTER XIII

THE ATOMIC HYPOTHESIS

To determine the nature of chemical phenomena requires, as we have found, very elaborate experimentation. And this has to be followed by still more elaborate reasoning before a systematic statement of the precise nature of the change can be made. Yet, when all this has been done, we are still unable to form a clear conception of what manner of procedure the change follows, for the *details* are entirely inaccessible to observation. We should like to know precisely how chemical union is consummated, and how chemical exchange is carried out. We should like to account for the fact that the automatically adjusted proportions of the materials used in every chemical change are entirely uninfluenced by temperature and other conditions. Above all, we should like to know, if possible, what state of affairs determines the employment of an individual unit weight by each element in all its combinations. None of these questions can be answered, however, because nothing can be seen which suggests any answer.

As usual in cases of this kind we construct an imaginary mechanism, a **formulative hypothesis** (p. 141) to account for the facts. In doing so, we are not under the illusion that we are discovering the actual machinery. We realize that we are simply making a sort of diagram which will assist our thought about the thing itself. Now a slight addition to the molecular hypothesis readily furnishes precisely what we need.

Atomic Hypothesis. — According to the molecular hypothesis, all matter is made up of small discrete particles, each of which has the same composition as has the body as a whole. It is difficult, therefore, to avoid the conception that the different materials in each compound molecule are more or less distinct entities also. Hence we make this the basis of a new hypothesis, and attribute to these constituent parts of molecules the properties of the chemical unit weights which are closely related to them. These parts must move from one state of

combination to another without alteration in their *mass*. Since they may be restored to their free condition and recombined as often as we choose, without impairment of their individuality, each kind must be composed of a *distinct variety of matter*. These two are almost the only qualities which the facts thus far presented justify us in attributing to them. We must, therefore, carefully avoid, for the present, the introduction of unnecessary complications by inventing for them any other properties gratuitously.

These parts of molecules which we thus suppose to be permanent, coherent masses, are named **atoms**. This word signifies objects which are not disintegrated (Gk. ἄτομος, uncut, *i.e.*, not yet cut). The relative weights of these imaginary masses are numerically the same as the chemical unit weights (p. 50), and hence, in terms of this hypothesis, we call the latter **atomic weights**.

It should be noted that although atoms, like molecules, are fictions, the atomic weights, since they are measured by experimental methods, are real. They originally received this name when Dalton, an English schoolmaster of Manchester, succeeded in unraveling the complications of the chemical composition of substances by the help of this very hypothesis, and realized for the first time (1805) that the possession by all elements of individual chemical unit weights lay at the basis of the whole system.

We may sum up all that the facts require us to assume about atoms by saying: **Atoms are the units of which molecules are aggregates. Those of like kind have equal masses, and differ from those of other kinds both in mass and the kind of material of which they are made.** The fundamentally different kinds of materials are the chemical elements. These statements include the whole atomic hypothesis.

It is to be noted, particularly, that there are no facts in chemistry which prove that atoms are *incapable of disintegration*. All we know is that in ordinary chemical changes they are transferred as wholes. It would only occasion the risk of conflict with facts still to be discovered if we elaborated our fiction any further than is absolutely necessary. Indeed, the phenomena of radio-activity have already compelled us to suppose that there are particles much smaller than atoms (see below). Without this assumption the new facts cannot be accounted for in harmony with the molecular hypothesis.

The idea that matter is composed of small particles is a very ancient one. Not even Dalton, however, although he used this conception continually as a means of thought about chemical and physical phenomena, made any distinction between atoms and molecules. This distinction was introduced later by Avogadro (1811). Yet, without this refinement, continual thought of the behavior of matter as consisting in transactions between small particles led Dalton to see that it was

probable that individual unit weights for each element must exist. The discovery that they did exist soon followed. The numbers which Dalton actually gave out, aside from the considerable experimental inaccuracies attached to them, were often equivalents and not modern atomic weights. It was after the publication of Dalton's ideas that Gay-Lussac discovered the law of combining volumes (1808), and until this law was discovered there was no criterion for fixing the values of the atomic weights. Gay-Lussac, at the end of his paper, pointed out that his discovery formed an important confirmation of Dalton's views. Strange to say, Dalton himself refused to accept Gay-Lussac's law, and so rejected the very means by which his own principle of chemical unit weights came eventually to be acknowledged as one of the foundation stones of the science. On the other hand, Dalton's fellow countrymen and contemporaries accepted the principle of unit weights, but rejected the atomic hypothesis by the help of which Dalton had reached them! Thus Sir Humphry Davy called them "proportions" instead of atomic weights, and Wollaston preferred the word "equivalents."

The Atomic Hypothesis and Chemical Change. — The change from chemical units to atoms is so slight that the application of this hypothesis to the description of chemical phenomena is very readily made. The description gains in concreteness, however, from the change. Thus, we consider iron from every source to be made of minute portions of iron matter which are all alike in weight, and presumably also in their other properties. Similarly, all specimens of sulphur are made of minute particles of sulphur having exactly the same weight. The weight of a sulphur atom, however, is different from that of an iron atom. When visible portions of the two substances unite, we conceive the operation to consist in the union of each atom of iron with one atom of sulphur to produce a molecule of ferrous sulphide. The consummation of this union between multitudes of pairs of the respective kinds of atoms in every second of time results in a chemical transformation whose progress is perceptible by the senses.

In more complex chemical changes, a further correspondence between the hypothesis and the facts comes to our notice. For example, when sulphuric acid acts upon sodium chloride to produce hydrogen chloride:

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4,$$

one part by weight of hydrogen takes the place of 23 parts by weight of sodium, and combines with 35.45 parts of chlorine to form the hydrogen chloride. This is the way we state the change when we refer to measurable quantities. According to this hypothesis, the operation consists in the repetition, millions of times over within a

small amount of material, of the substitution of one atom of hydrogen for one atom of sodium to form a molecule of hydrogen chloride. The special fact which we notice is that the atom of hydrogen suffices exactly to occupy the place of the atom of sodium. If it were too large, then a portion of each atom of hydrogen would remain unused, and so some free hydrogen would be produced along with the other products. If it were too small, then some atoms of hydrogen would be consumed in making up the material of the others to the right amount, and hence some chlorine might fail to receive any hydrogen in combination and escape in a free condition. Neither of these things is observed to take place, however. The remarkable fact about this, and all other double decompositions of the same sort, is that the little masses of the various elements exchange places without any alterations to fit the new compound being required. Hence our assumption that the atoms are permanent, coherent wholes. This, of course, is simply stating in terms of the atomic hypothesis the facts which underlie the conception of unit weights. **A chemical phenomenon** as we observe it, then, **is imagined to consist in some systematic liberation, combination, or exchange of atoms, according to a definite scheme, and repeated many millions of times (with every molecule) in a body or mixture of bodies.**

The Atomic Hypothesis and the Quantitative Laws. — The idea of atoms simply crystallizes somewhat more definitely the conception of chemical unit weights. Hence, it follows of necessity that the quantitative laws of chemical combination, out of which the latter arose, will be found to be entirely in harmony with the atomic hypothesis. The definite composition of each compound, for example, corresponds to the hypothesis that each substance is made up of a specific kind of molecules, all of which, in turn, contain the same kind and number of atoms.

The conception of valence (p. 101) suggests, in terms of this hypothesis, that some atoms unite with but *one* other atom, habitually ($NaCl$). Some, however, unite with two of the first kind ($ZnCl_2$), or with one other of their own kind (ZnO), still others with three atoms of the first kind ($AlCl_3$), and so forth. In other words, it involves the assumption that each kind of atom has a limited capacity for holding other atoms in combination. Thus, taking the most crudely mechanical view of the matter, we might elaborate the hypothesis by suggesting that there is a limit to the number of points at which

atoms may be attached to one another. When one atom of chlorine is attached to one of sodium, the combining capacity of each is exhausted. When one atom of hydrogen is attached to one atom of oxygen, one combining capacity still remains (H—O—), and can be satisfied by one more atom of hydrogen or of some other element.

The fact that the vapor density of the elements is often greater than that of the compounds in which they are contained, a fact which led us (p. 194) to the conception that there are two or more unit weights in one molecule, becomes more concrete in view of this hypothesis. It is as easy to understand that there may be two or more atoms of the *same* kind, as two or more of *different* kinds, united in one molecule.

Thus the general scheme according to which chemical changes occur, as well as all the quantitative relations in chemical phenomena, are admirably described when we think of those phenomena as constituted by transferences of atoms possessing definite weights.

Equations and the Atomic Hypothesis. — Since equations are simply *records* of the kinds and quantities of matter taking part in chemical changes, they require no addition to the atomic hypothesis. The symbols, which originally represented unit weights of the various elements, may stand equally well for atoms. Hence, in the current language of chemistry, potassium chlorate ($KClO_3$) is composed of one atom each of potassium and of chlorine and three atoms of oxygen in each molecule. The word "atom" stands for unit weight, and the word "molecule" for molecular weight.

Concretely, when these terms are used, the chemical equation represents one minute specimen of the change which is taking place throughout the whole mass. It shows enough molecules and atoms to furnish a complete example of what, repeated millions of times, will constitute a chemical change in a visible amount of material. There are a few details which this point of view suggests. For example, the equation $HgO \rightarrow Hg + O$ shows the weights, but does not include a complete sample of the materials in the point of view of this hypothesis. The smallest fragment of free oxygen which we can obtain is made of two atoms. Hence two molecules of mercuric oxide are required to furnish them. Thus the minimum number of *molecules* which would suffice for carrying out this change on a molecular scale is $2HgO \rightarrow 2Hg + O_2$. Similarly, since the smallest discrete

portions of free hydrogen and chlorine contain two atoms each, we must write the equation $H_2 + Cl_2 \rightarrow 2HCl$ (*cf.* p. 209).

May other Properties, Besides Definite Mass and Specific Material, be attributed to an Atom? — When this question is raised, the ground becomes less certain. A few examples will show the difficulties encountered and how far useful suggestions have been made.

Since mercury and iodine in a gaseous condition are composed of single atoms (p. 205), all atoms must be perfectly elastic just as molecules were assumed to be (p. 129). But this assumption is unnecessary in chemistry, for it throws no light upon chemical behavior.

The internal constitution of atoms remained for a century rather indefinite. As fictions, whose properties depended entirely upon those of the chemical units which they represented, they were not regarded as ever undergoing any change in the amount of material they contained. Recently, however, the peculiar radiations, which proceed from certain minerals containing uranium and thorium, have been discovered to be composed of minute particles (see Radium). It has been found possible, even, to estimate the size which these particles must possess as compared with atoms, in order that they may exhibit the properties which are peculiar to them. Different methods give somewhat different values. But it appears that some of these particles, which are called ***corpuscles*** (sometimes ***electrons***) to distinguish them from atoms, are of the same size from whatever element they are formed, and that their mass is about *one-thousandth of that of a hydrogen atom*. The relation is of this order, at all events. Their behavior also compels us to suppose that, even in the atom from which they issue, they are scattered at wide distances from one another. Thus, Professor J. J. Thomson suggests that, if the hydrogen atom were as large as a church, the thousand or so electrons which it contains might be compared to that number of full stops (.) scattered throughout the whole edifice. We have thus been compelled by the facts to add to the molecular hypothesis, first an atomic hypothesis, and then a ***corpuscular hypothesis.*** Our atoms turn out to be clusters of particles after all (p. 196). But the atom (chemical unit) of ordinary chemical change is not thereby affected, however many corpuscles may be thrust into it by other considerations.

In one direction, namely, that of accounting for the properties of compounds, no attempt has been made to adapt the atomic hypothesis so as to explain the facts. Thus, two hydrogen atoms in a molecule

give a gas almost insoluble in water; two chlorine atoms, a gas which is moderately soluble; but one of each gives hydrogen chloride, which dissolves in water in extraordinary quantities. So also, colorless substances give, by chemical union, strongly colored ones, and odorless substances, by chemical union, strongly odorous ones. Putting pieces of iron and sulphur side by side causes absolutely no change in the properties of either. And yet this hypothesis compels us to assume that if the particles are made fine enough, and placed close enough to one another, the individual properties of the constituents will entirely disappear. Hitherto we have failed to think of any qualities which might be attributed to the atoms in order to account for facts of this class. Why should oxygen (O_2) and ozone (O_3) be so different in behavior although the atomic theory hints at nothing but a substitution of three atoms for two? What atomic properties shall account for the difference between red and yellow phosphorus?

Usually, in explaining these matters, we forsake atoms and employ the conception of energy. We say that ozone has more energy than oxygen, and yellow phosphorus than red phosphorus. Here the conception of atoms as a means of accounting for properties is subordinate to that of energy. A tendency is plainly perceptible, indeed, not merely to supplement the atomic theory by the notion of energy, but to allow energy to supplant it entirely, and that not only in this but in other connections.

There are certain special peculiarities in the relation between composition and properties, however, to the explanation of which the atomic theory has been successfully adapted. Thus, certain compounds precisely similar in composition, such as barium peroxide (BaO_2) and lead dioxide (PbO_2), show entirely different chemical behavior. The former of these when treated with an acid gives hydrogen peroxide (*q.v.*), while the latter gives only water and oxygen. If it is merely a question of composition, the substances should behave alike. So, also, we often have two or more compounds identical in molecular weight, and in the elements and numbers of units which they contain, which are nevertheless totally different in physical and chemical properties. To account for this difference we have found it convenient to suppose that, although the atoms contained in the two or more kinds of molecules are of the same numbers and kinds, **they are in different geometrical arrangement towards one another** (see Urea). Sometimes one of these substances can be made directly from the other, and this gives us that variety of chemical change which was named

"internal rearrangement" (p. 15). In discussing facts like the above in terms of the atomic hypothesis we speak of the **structure** of the molecule and the **constitution** of the substance, and, to represent our conclusions, we use graphic formulæ (see Constitutions of oxygen acids of chlorine, hydrogen peroxide, sulphuric acid, formic acid and urea).

It is becoming increasingly difficult to maintain the distinction which formerly seemed very clear between physical and chemical phenomena. The atomic hypothesis serves the purpose in a rough way for the simpler cases. If the atoms are undisturbed, and therefore the chemical properties remain unchanged, the substance has undergone a physical change only. If, however, the atoms are altered in their relations to one another, either by rearrangement, or in some more drastic manner, the change is a chemical one. Now, however, so many shades of difference among the examples that come under the head of internal rearrangement have been found, that the atomic hypothesis is applied with constantly increasing difficulty (*cf.* p. 16). Whether it will be possible to apply this hypothesis consistently in this region remains yet to be seen.

Summing this up, we find that all the suppositions the chemist makes are: That an atom has a specific mass and consists of a specific kind of material, and, sometimes, that the atoms in a molecule are arranged with reference to one another in space in some definite way. After making this formulative hypothesis, however, he *knows* no more than he did before about the *real* mechanism of chemical change.

Is the Atomic Hypothesis a Fact.—The language of chemists has become so saturated with the phraseology of the atomic and molecular hypotheses, that we speak in terms of atoms and molecules as if they were objects of immediate observation. It must be reiterated, therefore, that this language is figurative, and must not be taken literally. The atomic hypothesis provides a convenient form of speech, which successfully describes many of the facts in a metaphorical manner. But the handy way in which the atomic hypothesis lends itself to the representation of the characteristic features of a chemical change falls far short of constituting a proof that atoms have any real existence. The restatements which we have made of some of the characteristics of chemical change in this chapter depend upon the continued reign of the atomic hypothesis. The definitions of the same things given previously were based upon experiment and are of permanent value, so that no question can be allowed to arise as to which of the two definitions in each case is the more important one.

The existence of the unit weights (atomic weights) will probably appear to come nearer to furnishing verification of the hypothesis that matter is composed of atoms than any other fact. It may seem unthinkable that each element should use the same proportions by weight in entering into many different combinations if it is not actually done up in packets whose weight is represented by this number. Such an inference, however, is not really justified. An illustration will make this clear. If we were unable to see wheat close at hand, so as to distinguish its structure, and

our information was confined to observation from a distance and the reading of market quotations, we should be led to infer from the latter that it was a substance which was always done up in bushels. Yet we know that this inference would be entirely incorrect. The substance really exists in the form of bushels *at the moment of measurement only*. So there might be imagined properties, at present unknown to us, which directed the quantitative selection of material for chemical change and rejected the excess, without the existence of any permanent segregration into pieces of unalterable dimensions. The only bushels and ounces which we have are in the measuring apparatus and not in the material measured ; so the only atomic weights may be in the properties controlling chemical combination, and not in the matter combining.

Exercises. — 1. In previous chapters our definitions have been experimental. In imitation of the definitions of the law of definite proportions and of valence (p. 220), give theoretical definitions of the following, in terms of the atomic hypothesis: Physical and chemical phenomenon, multiple proportions, chemical unit weight, molecular weight, element, compound, symbol, formula, equation.

2. Criticize the definitions : The atomic weight of an element is the smallest portion of that element which takes part in chemical change. An atom is the smallest particle that can be conceived.

3. Define all the varieties of chemical change (p. 187) in terms of the atomic hypothesis.

CHAPTER XIV

THE HALOGEN FAMILY

THE elements to which we have so far devoted most attention have been oxygen, hydrogen, and chlorine. If we recall the chemical properties and relations of these elements we shall recognize the fact that they all possess very distinct individualities.

The Chemical Relations of Elements. — Hydrogen is the substance (p. 109) which unites readily with oxygen and chlorine, less readily with other non-metals, and scarcely at all with metals. Oxygen and chlorine resemble one another somewhat in the greatness of their chemical activity and the variety of free elements with which they are capable of uniting, but differ markedly in what we have called their chemical relations (p. 177). The resulting compounds belong, in fact, to quite different classes — oxygen forms oxides, chlorine forms chlorides — **and elements are considered similar only when they resemble one another in chemical relations, and produce, by combination with the same element, compounds having similar chemical properties.** Thus the common oxide of hydrogen, water, is a neutral substance, and is chemically rather indifferent. The chloride of hydrogen in aqueous solution is a strong acid and is chemically very active.* If all the other chemical elements differed from one another as much as do these three, the study of the chemical elements would be tedious and tiresome, since we should be denied the satisfaction of tracing resemblances, and the elements would be incapable of classification. In reality, however, we find that they are not incapable of being grouped together in sets. They are classified according to the kind of substances with which they combine and the chemical nature of the products. In some families the resemblance is close, in others less close.

* The difference between oxides and chlorides is seen in their behavior, and will show itself as we proceed. We have already learned, however, that oxides often unite with water to form acids or bases (p. 119). Chlorides do not unite with water to form new substances with marked characteristics (*cf.* p. 121). They belong to the large class of compounds designated **salts** (*q.v.*).

The present group is of the former class, and will serve, therefore, as a convenient beginning in the work of tracing relations between the elements and in classifying the facts of descriptive chemistry.

The Chemical Relations of the Halogens.— The bromide (NaBr), iodide (NaI), and, to a less extent, the fluoride (NaF), of sodium, resemble sodium chloride (NaCl) in appearance and behavior. From the fact that chlorine, bromine, iodine, and fluorine are thus all able to produce substances like salt without the presence of any other constituents, they are known as the **halogens** (Gk. ἅλς, salt; γεννᾶν, to produce), and their compounds are named the **halides**. The halogens, as the above formulæ show, are univalent. They all form compounds with hydrogen, and these compounds closely resemble hydrogen chloride (*q.v.*). For example, they are colorless, they are gases (with the exception of hydrogen fluoride which is a very volatile liquid), they are very soluble in water, and their solutions are acids. Other relations will be given in a summary at the end of the chapter.

BROMINE.

Occurrence. — The compounds of chlorine, bromine, and iodine usually occur together in nature, while the compounds of fluorine are not found in the same sources. Bromine occurs chiefly in the form of the bromides of sodium and magnesium, in the upper layers of the natural beds of rock salt.

Preparation. — In the chemical point of view there are three distinct ways in which bromine is made. The first of these is closely related to the common method of preparing chlorine (p. 172). As hydrobromic acid, unlike hydrochloric acid, is not formed extensively in connection with any chemical industry, potassium bromide, the most accessible compound of bromine, is treated with concentrated sulphuric acid, and the product is oxidized with powdered manganese dioxide in one operation. The whole action may be represented in a single equation (see next section), as follows:

$$2KBr + 3H_2SO_4 + MnO_2 \rightarrow MnSO_4 + 2KHSO_4 + 2H_2O + Br_2.$$

Bromine being a volatile liquid, while the two sulphates are involatile, its vapor passes off along with a little water when the above mixture is heated. It is condensed in a worm-tube surrounded by cold water.

The second method of preparing bromine depends on the fact that chlorine is a more active element and displaces bromine from combination. When, therefore, chlorine is passed into a solution of potassium or sodium bromide, potassium or sodium chloride is formed and the bromine liberated:

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2.$$

When the liquid is warmed, the bromine passes off along with a part of the water, and may be condensed as before.

Aqueous solutions of soluble bromides may be decomposed by means of a current of electricity. The bromine is set free at the positive electrode.

The whole of the bromine used in commerce is at present manufactured in the first two of these ways. Two-thirds of the supply is obtained from Stassfurt, where, after the extraction of the potassium chloride from the impure carnallite ($KCl, MgCl_2, 6H_2O$), the mother-liquid is found to contain the more soluble sodium and magnesium bromides in considerable quantities. The warm mother-liquor trickles down over round stones in a tower. The chlorine is introduced from below and dissolves in the liquid. The bromine is thus liberated and passes off as vapor. A part of our supply of bromine is obtained from the brines of Ohio, West Virginia, and Kentucky. Here the liquid, after most of the common salt has been removed by crystallization, is assayed to ascertain the quantity of bromine which it contains, and is treated with the calculated amount of sulphuric acid necessary for the action. Manganese dioxide is then added in small quantities at a time. In Michigan the brines are treated with electrolytic chlorine. The quantity produced in America in 1904, was 897,100 pounds, and was valued at $269,130.

A Plan for Making Very Complex Equations. — When an equation involves more than two initial substances or products, as does the one given above for the first method of preparing bromine, it cannot readily be worked out by the method formerly recommended (p. 110). After the formulæ of all the substances, on both sides, have been set down, it is difficult to hit upon the proper numerical factors required to balance the equation. In such cases a good plan is to select two of the initial substances and make a **partial equation** showing part of the action and including at least one actual product. Any unused units (not constituting a product) are then set down also and treated as a

balance. Thus the first two of the substances, in the above equation, will furnish the second of the products:

$$KBr + H_2SO_4 \rightarrow KHSO_4 \ (+ \ HBr). \qquad (1)$$

Then we may represent the formation of the first of the products from the materials which evidently must have been used up in forming it, and set down the balance as before:

$$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O \ (+ \ O). \qquad (2)$$

We then perceive that the last of the products might come from the oxidation of the first balance by the second:

$$(2HBr) + (O) \rightarrow H_2O + Br_2. \qquad (3)$$

The third partial equation shows that 2HBr will be needed for the amount of O obtainable from MnO_2, so we take enough of the material in (1) to get the required 2HBr:

$$2KBr + 2H_2SO_4 \rightarrow 2KHSO_4 \ (+ \ 2HBr). \qquad (1)$$

When we now add the real substances used and produced, as they occur in these partial equations, and leave out the balances, which have been adjusted so as to cancel one another, we obtain the final equation already given for the action. It must be observed that this subdivision of the action into parts is a purely arithmetical device, used solely to simplify the arithmetical process of writing the equations, and is not intended to imply that the chemical change itself follows these or, indeed, any stages. It happens that the three partial equations we have used in this illustration all represent interactions which can take place separately. But the arithmetical value of the device does not depend upon this. The partial equations made for purposes like the present one are often purely fictitious. It is still true, however, that we are aided in the selection of partial actions at each step by following some plausible theory as to stages for the action which, if there were any, would be chemically conceivable.

Physical Properties. — Bromine is a dark-red liquid (sp. gr. 3.18). It boils at 59°, forming a deep-red vapor, and even at ordinary temperatures gives a high vapor pressure (150 mm. at 18°) and evaporates quickly. When cooled it forms red, needle-shaped crystals, which melt at 7.3°. A saturated aqueous solution (bromine-water) at ordinary temperatures contains about three parts of bromine in one hundred of

water. The element is much more soluble in carbon bisulphide, alcohol, and other organic solvents. Its vapor density up to 750° is 160 (oxygen = 32).

Bromine (Gk. βρῶμος, a stench) has a most pungent odor. It has a very irritating effect on the mucous membrane of the nostrils and throat. If spilled upon the hands it has a most destructive action upon the tissues.

When free bromine is added to starch emulsion no special change in tint is observable unless a very large amount of the element is used (see Iodine).

Chemical Properties. — The molecules of bromine are much less stable than those of hydrogen, oxygen, or nitrogen. The atomic weight of bromine is 79.96, so that in the form of vapor it has two atoms in a molecule, and is represented by the formula Br_2. At 1050° the vapor density is 150.5, and dissociation into Br has begun.

Like chlorine, it forms an unstable hydrate with water.

Bromine unites directly with hydrogen. The mixture of the gases is not explosive, and the union is much slower than in the case of chlorine. In presence of finely divided platinum the speed of the action may be considerably increased.

Bromine forms compounds directly, both with non-metals, like phosphorus and arsenic, and with most of the metals. Towards unsaturated substances and organic compounds it behaves like chlorine (*q.v.*). In all cases the interaction is less violent than when chlorine is used, and the element is displaced from combination with hydrogen and with the metals by free chlorine.

Potassium bromide is employed in making photographic plates and in medicine. Bromine is required in large quantities in the manufacture of intermediate products used in the preparation of organic dyes.

Hydrogen Bromide.

Preparation. — It might be expected that the most convenient way of producing this compound would be similar to that used in preparing hydrogen chloride, namely, by the action of concentrated sulphuric acid upon some common bromide such as potassium bromide ($KBr + H_2SO_4 \rightleftarrows HBr + KHSO_4$). We find indeed that at first a colorless gas is given off, which fumes strongly in the air just like hydrogen chloride, and is the required substance. Almost immediately, how-

ever, this gas acquires a yellow and then a brown tinge, and we discover that free bromine is being produced at the same time. If we examine the gas still further, we recognize also the presence of sulphur dioxide. It is impossible, therefore, to produce hydrogen bromide free from those two impurities by this action.

The origin of the bromine and sulphur dioxide which complicate this chemical change may readily be traced. Hydrogen bromide is less stable than hydrogen chloride, and its hydrogen can more easily be removed by the action of substances containing oxygen. In this case the sulphuric acid acts as the oxidizing agent, yielding oxygen, sulphur dioxide, and water ($H_2SO_4 \rightarrow O + SO_2 + H_2O$). Thus the two extra gaseous products are seen to be formed by a change proceeding parallel with the main action:

$$2HBr + H_2SO_4 \rightarrow 2H_2O + SO_2 + Br_2.$$

The **simultaneous occurrence**, in this fashion, **of two** more or less **independent actions** is not uncommon. The speeds of such actions may be differently affected by temperature. Thus, here, the second action seems to become more extensive as the temperature rises (see Chap. xvi). Since all acids decompose all salts more or less, by use of an acid which does not give up its oxygen so readily, such as phosphoric acid, pure hydrogen bromide may be obtained ($KBr + H_3PO_4 \rightarrow HBr + KH_2PO_4$). The small solubility of the salt in concentrated phosphoric acid retards the interaction (p. 179) and makes the evolution of the gas very slow, however.

Pure hydrogen bromide is prepared by hydrolysis (p. 181) of phosphorus tribromide. When bromine and phosphorus are mixed, a violent union of the two elements takes place, producing phosphorus tribromide (PBr_3). This substance, which is a colorless liquid, is in turn broken up with great ease by water, producing phosphorous acid, which is not volatile, and hydrogen bromide:

$$P\begin{cases} Br \\ Br \\ Br \end{cases} + \begin{matrix} HOH \\ HOH \\ HOH \end{matrix} \rightarrow P(OH)_3 + 3HBr.$$

In practice, those two actions are carried on simultaneously. To diminish the vigor of the interaction, red phosphorus is taken instead of yellow, and is mixed with two or three times its weight of sand in a flask (Fig. 70). A small quantity of water is added. Excess of water must be avoided, as the hydrogen bromide produced is extremely

soluble, and would therefore be retained in the flask instead of being disengaged as gas. The bromine is placed in the dropping funnel, and admitted, a little at a time, to the mixture. The gas produced is passed through a U-tube containing glass beads mixed with red phosphorus. The latter combines with any bromine which may have escaped chemical change and have been carried along with the gas. The second U-tube, containing water, may be attached when a solution of the gas is required.

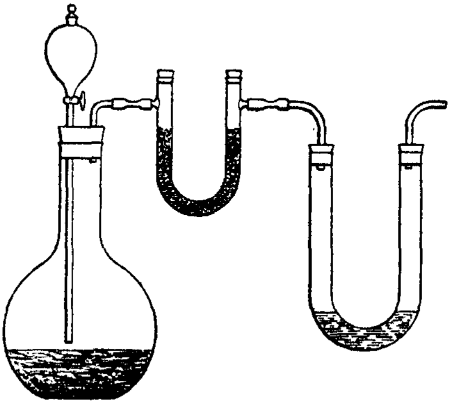


FIG. 70.

Physical Properties. — Hydrogen bromide is a colorless gas with a sharp odor. It is two and a half times as heavy as air. It is easily reduced to the liquid condition. It is exceedingly soluble in water, and in contact with moist air condenses the water vapor to clouds of liquid particles. When distilled, the solution in water behaves like that of hydrogen chloride (p. 182). It loses mainly either water or hydrogen bromide, according as it is dilute or exceedingly concentrated, until an acid of constant boiling-point (126° at 760 mm. pressure), containing 48 per cent of hydrogen bromide, passes over.

Hydrogen bromide, whether in the gaseous condition or in the liquefied form, is a nonconductor of electricity.

Chemical Properties. — The chemical properties of hydrogen bromide are similar to those of hydrogen chloride (p. 183). It is somewhat less stable, and dissociation into its constituents begins to be noticeable at 800°. When free from water, it is not an acid (see below), and is not very active chemically, although it behaves towards some metals much like hydrogen chloride. When the solution in water is strongly cooled, crystals of a definite hydrate ($HBr, 2H_2O$), corresponding to that of hydrogen chloride, are obtained. When the gas is mixed with chlorine, hydrogen chloride and free bromine are instantly produced, and much heat is evolved by the change, $2HBr +$

$Cl_2 \rightarrow 2HCl + Br_2$. The heat produced by the union of hydrogen and bromine vapor is 12,100 calories. This is much less than the amount produced by the union of chemically equivalent quantities of hydrogen and chlorine (22,000 calories). When chlorine displaces bromine from hydrogen bromide, the heat evolved is found to be the difference between these two numbers. Using the rule of constant heat summation (p. 78), we write equation (2) so that HBr is on the same side with Cl (with which it interacts), and the products of the equation required (HCl and Br) are both on the right:

$$H + Cl \rightarrow HCl + 22{,}000 \text{ cal.} \quad (1)$$
$$HBr \rightarrow Br + H - 12{,}100 \text{ cal.} \quad (2)$$
$$\text{Adding,} \quad HBr + Cl \rightarrow HCl + Br + 9900 \text{ cal.}$$

The 12,100 calories are produced by the union of gaseous bromine with hydrogen, and the final result is, therefore, that for the production of *gaseous* bromine. If the heat of formation of liquid bromine is required, the latent heat of vaporization of bromine (7296 calories), which will be evolved when the element condenses, must be added.

Chemical Properties of Hydrobromic Acid.— The solution of the hydrogen bromide in water is an active acid (*cf.* p. 111). It conducts electricity extremely well. In contact with metals, oxides of metals, and hydroxides of metals, it behaves exactly like hydrochloric acid (p. 185). In the first case, hydrogen is set free and the bromide of the metal produced. In the other two cases, water and the bromides of the metals are produced. Oxidizing agents set bromine free from hydrobromic acid, and the only difference as compared with hydrochloric acid is that less powerful oxidizing agents can produce this result. Chlorine dissolved in water displaces bromine from hydrobromic acid and from soluble bromides with ease.

IODINE.

Occurrence.—Iodine, like bromine, occurs in sea-water, although it is present in much smaller quantities. Fortunately, certain species of sea-weed seem to have the power to remove it from water, and use it as a constituent in complex organic compounds which they contain. In the case of certain species, the ash of the sea-weed is said to contain as much as two per cent, or even more. The other chief source of iodine is in Chili saltpeter ($NaNO_3$), in which it is present in the

form of small proportions of sodium iodate ($NaIO_3$) and sodium iodide. Of recent years the quantity obtained commercially from this source has greatly increased, while that from sea-weed has diminished.

It is worth noting that while the total amount of iodine found in the human body is small, the proportion contained in the thyroid gland is considerable. A complex organic substance, known as iodothyrin, has been extracted from sheep's thyroids. It is administered with marked success in certain diseases, such as cretinism, which are associated with very small development of this gland.

Preparation. — In factories where the iodine is extracted from sea-weed, the latter is first burned, either roughly in hollows in the ground, or more carefully in specially constructed ovens. A great deal of the iodine seems to be lost by volatilization in this process, but the ash which remains, and which is known in Scotland as *kelp* and in Normandy as *varec*, still contains from 0.5 to 1.5 per cent of sodium iodide. The ash is treated with water, and the solution is evaporated so as to permit the deposition of the sodium chloride and sodium sulphate which it contains. The sodium iodide, being very soluble, remains in the mother-liquor. This is then treated with manganese dioxide and sulphuric acid. The quantity of manganese dioxide is carefully measured so as to be just sufficient to set free the iodine contained in the liquid without proceeding farther to the liberation of the chlorine which it contains in much larger amounts. When the mixture is heated, the iodine passes off in the form of vapor, and is condensed in a suitable receiver. The action (*cf.* pp. 227, 229) is:

$$2NaI + MnO_2 + 3H_2SO_4 \rightarrow MnSO_4 + 2NaHSO_4 + 2H_2O + I_2.$$

In France the treatment is similar, excepting that chlorine is used to liberate the iodine in the last stage ($2NaI + Cl_2 \rightarrow 2NaCl + I_2$). The quantity is adjusted so that excess may not be employed. This is to avoid the formation of a compound of chlorine and iodine, which easily arises by direct union of the elements. The iodine, being insoluble, forms a dense precipitate, and, when the liquid is pressed out, it remains behind in the form of a paste. Electricity could also be used for the decomposition of this mother-liquor. The iodine is set free at the positive electrode, while the metals pass to the other. This process does not, however, seem as yet to have found actual application in commerce.

In all cases the iodine is subjected to purification before being sold. This is carried out by distilling it with a little powdered potassium

iodide. It condenses in the solid form directly, in glittering black plates (sublimed iodine). The distillation of a solid body, when a condensation takes place directly to the solid form, is spoken of as **sublimation.**

Physical Properties.—Iodine (Gk. ἰοειδής, like a violet) is a solid substance (sp. gr. 5), exhibiting large crystalline plates of rhombic form. It melts at 114°, and boils at 184°. The vapor has at first a reddish-violet tint, and on being more strongly heated becomes deep blue.

Iodine is much less soluble in water than are the other halogens, and the solution has a scarcely perceptible brown tint. At ordinary temperatures one part of iodine dissolves in about 5000 to 6000 parts of water. It is much more soluble in carbon disulphide (p. 156) and in chloroform, in which it gives violet solutions. In alcohol it gives a solution which is brown. The brown color is attributed to the fact that in alcohol the iodine is in a condition of feeble combination and not simply in solution. An aqueous solution of potassium iodide, hydrogen iodide, or any other iodide, has likewise the power to take up large quantities of iodine. In these cases, however, the formation of definite compounds (such as, $KI + I_2 \rightleftarrows KI_3$), by a reversible action, accounts for the amount of iodine which appears to be dissolved.

The behavior of free iodine towards starch forms a distinctive test for both substances (*cf.* p. 99). When starch is treated with boiling water it passes into a state of fine suspension, and the liquid may be filtered without removal of all the starch. When traces of iodine, contained, for example, in the pale-brown aqueous solution, are added to this filtered starch emulsion, a deep-blue color is produced. The same action is used as a test for starch. This blue substance is not a chemical compound, but a solution of the iodine in the solid starch which is suspended in the water. That the color becomes so much stronger is in harmony with the fact that dissolved bodies frequently confer a tint different from their own upon their solutions.

Chemical Properties.—The molecular weight of iodine, ascertained by weighing the vapor at a temperature above the boiling-point, is 254.8. The atomic weight being 126.97, the molecule contains two atoms. This value for the density remains unchanged when the measurement is made at temperatures up to about 700°. Beyond this point, however, the vapor diminishes in density more rapidly than

Charles' law would lead us to expect, and at 1700° the molecular weight has fallen to 127. As the vapor is heated, a larger and larger proportion of the molecules is broken up, until the decomposition has become complete. As in all cases of dissociation, when the vapor is cooled the atoms recombine to form molecules. This chemical action is interesting, since it is the most notable case in which we encounter both the monatomic and the diatomic forms of the same element. The heat given out when the atoms reunite to form the molecules is very considerable ($2I \rightleftarrows I_2 + 28{,}500$ cal.), indicating that the chemical union of two atoms of identical nature may be as vigorous as that of two atoms of different chemical substances. The monatomic and diatomic forms of iodine should be distinct chemical substances, and if the investigation of the behavior of the former were not hampered by the very high temperature at which alone it exists, it would doubtless be found to exhibit different chemical properties.

Iodine forms no hydrate with water. It exhibits little tendency to unite with hydrogen. Iodine unites directly with a number of elements, including some non-metals and the majority of the metals. When phosphorus is presented in the yellow form, the action takes place spontaneously without the assistance of heat. Both chlorine and bromine displace iodine from combination with hydrogen and the metals ($2HI + Br_2 \rightarrow 2HBr + I_2$). The action may be brought about either with the substances in dry form or with their aqueous solutions.

Iodine in water, like chlorine in water, constitutes an oxidizing agent, although the former is much the feebler of the two. It converts, however, sulphurous acid (*q.v.*) into sulphuric acid. The action, so far as the iodine and the water are concerned, is shown by the partial equation

$$I_2 + H_2O \rightarrow 2HI (+ O).$$

This action does not take place, however, excepting in presence of a body capable of assisting in the reduction of the water and of uniting with the oxygen. In analytical chemistry a solution of iodine in potassium iodide containing a known proportion of iodine (a **standard** solution) is used for estimating the quantity of an oxidizable substance present in a given specimen. The amount of oxidizable substance present is measured by the quantity of the standard iodine solution which can be decolorized and suffer removal of its iodine. This method is known as **iodimetry.**

Iodine and its compounds are much used in the arts and medicine.

Iodine is applied, in the form of an alcoholic solution ("tincture of iodine"), for the reduction of some swellings. It is required in making iodoform (CHI_3), and the iodides of potassium, rubidium, and sodium, which are used in medicine. Potassium iodide is likewise employed in the manufacture of photographic plates. Large quantities of iodine find application in the color industry for making intermediate products needed in the manufacture of aniline and other organic dyes.

HYDROGEN IODIDE.

Preparation.—The direct union of hydrogen and iodine cannot be employed in preparing pure hydrogen iodide. The union takes place slowly, and, since the action is markedly reversible (*cf.* p. 176), always remains incomplete: $H_2 + I_2 \rightleftarrows 2HI$. In presence of finely divided platinum the union, so far as it is capable of proceeding, may be hastened, but the amount of the compound formed is not greater. At 448°, for example, 79 per cent of the constituents unite, and the remainder is unaffected either by longer heating or by platinum. At other temperatures the proportion is different, but at none is the action complete. Hydrogen and iodine unite with little vigor because the union is not accompanied by a sufficiently marked liberation of energy (*cf.* HCl, p. 233). Thus at 18° the action is really endothermal (– 6100 calories for HI), and at 400°, although the action is exothermal, only 535 calories of heat are set free.

The action of concentrated sulphuric acid upon potassium or sodium iodide is equally inapplicable. In this case, as in that of hydrogen bromide (p. 231), the hydrogen halide reduces the sulphuric acid, and much free iodine is formed. Here, on account of the greater instability of hydrogen iodide and the greater ease with which it parts with its hydrogen, the reduction of the sulphuric acid is much more complete, the primary product being apparently hydrogen sulphide. The actions, which proceed simultaneously (p. 231), are:

$$KI + H_2SO_4 \rightleftarrows HI + KHSO_4 \text{ and } H_2SO_4 + 8HI \rightarrow H_2S + 4H_2O + 4I_2.$$

As soon as the heat produced by the action has raised the temperature sufficiently, hardly any of the hydrogen iodide escapes oxidation.*

* When much sulphuric acid is used, sulphur dioxide and free sulphur are formed also. This is in consequence of a secondary action of the hydrogen sulphide on the sulphuric acid, and of the sulphur dioxide so formed upon the excess of hydrogen sulphide (see Hydrogen sulphide):

$$H_2S + H_2SO_4 \rightarrow 2H_2O + S + SO_2, \qquad SO_2 + 2H_2S \rightarrow 3S + 2H_2O.$$

Finely powdered sodium iodide and concentrated phosphoric acid (*cf.* p. 179), when mixed and warmed, give pure hydrogen iodide ($NaI + H_3PO_4 \rightleftarrows HI\uparrow + NaH_2PO_4$). This action was formerly used in preparing the gas.

The best method is one similar to that described under hydrogen bromide. Phosphorus and iodine unite directly to form PI_3. This is a yellow solid which is violently decomposed by water and gives phosphorous acid and hydrogen iodide:

$$PI_3 + 3H_2O \rightarrow P(OH)_3 + 3HI.$$

If excess of water, which dissolves hydrogen iodide, is avoided, the latter goes off in a continuous stream in a gaseous condition.

Still another method of making hydrogen iodide is frequently employed when a solution of the gas in water is required, and not the gas itself. Powdered iodine is suspended in water, and hydrogen sulphide gas (*q.v.*) is introduced through a tube in a continuous stream. The iodine dissolves slowly in the water, I_2 (solid) $\rightleftarrows$ I_2 (diss'd), and acts upon the hydrogen sulphide, which likewise dissolves, H_2S (gas) $\rightleftarrows$ H_2S (diss'd). Sulphur separates in a fine powder, S (diss'd) $\rightleftarrows$ S (solid), and hydrogen iodide is formed in accordance with the equation:

$$H_2S + I_2 \rightarrow 2HI + S.$$

This action takes place, however, only in presence of water, although the water does not appear in the equation. The solution is freed from the deposit of sulphur by filtration, and may be concentrated to 57 per cent of hydriodic acid by distilling off the water.

The theory of the last method is worthy of attention. It will be seen that while iodine has little tendency to unite with free hydrogen, it is here able to decompose a compound containing hydrogen, in order to secure this element. It is enabled to do this by the fact that the very large amount of heat given out by the mere solution of hydrogen iodide in water converts the action, which would otherwise be endothermal, into an exothermal one. In the absence of water, the reverse of the above action takes place with ease. In presence of water, however, the great heat of solution (p. 164) of the hydrogen iodide (+ 19,200 cal.) more than balances the heat absorbed by the chemical change, and the action as a whole takes place with evolution of heat (see, also, Preparation of hydrogen sulphide).

Physical Properties. — Hydrogen iodide is a colorless gas with a sharp odor. Its molecular weight is 128, and it is therefore much heavier than air, the average weight of whose molecules is 28.955 (p. 193). It is a nonconductor of electricity, both in the gaseous and in the liquefied conditions. It is exceedingly soluble in water, so that at 0° ten grams of water will absorb ninety grams of the gas, giving a 90 per cent solution. The behavior of this solution is similar to those of hydrogen chloride and hydrogen bromide (*cf.* pp. 182, 232). The mixture of constant boiling-point distils over at 127° (at 760 mm.), and contains 57 per cent of hydrogen iodide.

Chemical Properties. — Hydrogen iodide is the least stable of the hydrogen halides. When heated it begins visibly to decompose into its constituents at 180°. On account of the ease with which it parts with the hydrogen which it contains, it can be burned in oxygen gas, $4HI + O_2 \rightarrow 2H_2O + 2I_2$. When the gas is mixed with chlorine, a violent chemical change, accompanied by a flash of light, occurs, the iodine is set free, and hydrogen chloride is produced, $Cl_2 + 2HI \rightarrow 2HCl + I_2$. Bromine vapor will similarly displace the iodine from hydrogen iodide.

Chemical Properties of Hydriodic Acid. — In most respects the aqueous solution behaves exactly like hydrochloric and hydrobromic acid. With oxidizing agents, for example, such as manganese dioxide, it gives free iodine, just as the others give free chlorine and bromine respectively. Here, however, the oxidation is so much more easily carried out, that it is slowly effected by atmospheric oxygen, so that hydriodic acid left exposed to the air gradually becomes brown ($O_2 + 4HI \rightarrow 2\,H_2O + 2I_2$). The free iodine which is produced, remains dissolved in the hydrogen iodide, probably in the form of a compound HI_3. Finally, however, the free iodine as its quantity becomes greater, and that of the hydrogen iodide smaller, is deposited in crystalline condition. On account of the ease with which hydriodic acid parts with its hydrogen, it is frequently used in chemistry as a reducing agent.

Although the dry gas is not an acid, the solution has all the ordinary properties of this class of substances (*cf.* p. 92). The hydrogen may be displaced by metals like zinc and magnesium. The acid interacts with oxides and hydroxides, forming iodides and water.

Fluorine.

The discussion of this element should logically have preceded that of chlorine, since it is of all the members of the halogen family the most active. Chlorine was taken up first, however, because its compounds are more familiar. Fluorine is found in combination in nature. It occurs chiefly in the mineral fluorite (calcium fluoride, CaF_2) and in cryolite, a double fluoride of aluminium and sodium (AlF_3, $3NaF$).

Preparation. — When a solution of hydrofluoric acid is heated with manganese dioxide, oxidation does not occur and free fluorine is not produced. Until very recently all efforts to isolate the element failed. It was perfectly understood that the reason of these failures lay in the greater chemical activity of fluorine, which made it more difficult of separation from any state of combination than the other halogens. Its preparation was finally achieved by Moissan (1886) by the decomposition of anhydrous hydrogen fluoride, which is liquid below 19°, by means of electricity. The apparatus (Fig. 71) is made of copper, which, after receiving a thin coating of the fluoride, is not further affected. To reduce the tendency to chemical union, the whole is immersed in a bath giving a temperature of − 23°. The electrodes are made of an alloy of platinum and iridium, which is the only substance that can resist the action of the fluorine when freshly liberated by the electric current. Hydrogen fluoride, like other hydrogen halides, is a nonconductor of electricity, and a small quantity of potassium fluoride has to be added to enable the current of electricity to pass. The fluorine is set free at the positive electrode, and hydrogen appears at the negative. The U-tube is closed after the introduction of the hydrogen fluoride by means of blocks made of calcium fluoride, which is naturally unable further to enter into combination with fluorine. For the reception and examination of the fluorine gas, other copper tubes can be screwed on to the side necks of the apparatus, and, when necessary, small windows of calcium fluoride

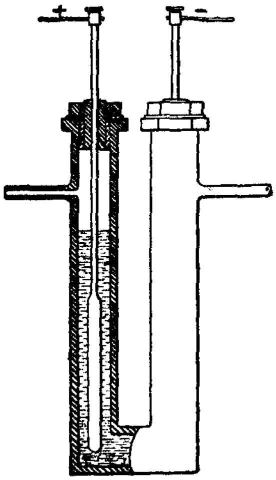


Fig. 71.

can be provided. It has been found that fluorine dried with extraordinary precautions is without action on glass.

Physical Properties. — Fluorine is a gas whose color is like that of chlorine, but somewhat paler. Its density has not been measured with great exactitude, but the value obtained indicates a molecular weight of 38, showing that there are two atoms in the molecule (the atomic weight is 19). The gas is the most difficult of the halogens to liquefy. The liquid boils at − 186°.

Chemical Properties. — Fluorine unites with every element, with the exception of oxygen, and in many cases does so with such vigor that the union begins spontaneously without the assistance of external heat. Dry platinum and gold are the elements least affected. It explodes with hydrogen at the ordinary temperature, without the assistance of sunlight. Fluorine displaces oxygen from water instantaneously and gives ozone (*q.v.*). On the introduction of a drop of water into a tube of fluorine the vessel is filled with the deep-blue gas, $3F_2 + 3H_2O \rightarrow 3H_2F_2 + O_3$.

The chlorine in hydrogen chloride is displaced by fluorine as easily as chlorine in turn displaces bromine or iodine.

Hydrogen Fluoride.

Preparation. — Pure, dry hydrogen fluoride is best made by heating potassium hydrogen fluoride, $2KHF_2 \rightleftarrows 2KF + H_2F_2\uparrow$. For ordinary purposes, however, the preparation of an aqueous solution is the ultimate object. Usually powdered calcium fluoride is treated with concentrated sulphuric acid, and the mixture distilled in a platinum retort:

$$CaF_2 + H_2SO_4 \rightleftarrows CaSO_4 + H_2F_2\uparrow.$$

The hydrofluoric acid passes over and is caught in distilled water. The aqueous solution thus obtained has to be kept in vessels made of lead, rubber, or paraffin, as glass interacts with the acid with great rapidity (see below).

Physical Properties. — Hydrogen fluoride is a colorless liquid, boiling at 19.4°. It mixes freely with water, and, on distillation, an acid of constant boiling-point (120° at 760 mm.) containing 35 per cent of hydrogen fluoride is obtained. The vapor density of the

hydrogen fluoride between its boiling-point and 30° corresponds to a molecular weight of 40, and the formula should therefore be H_2F_2. Above this temperature the vapor becomes lighter (p. 207), and, when 88° is reached, the molecular weight has fallen to 20, corresponding to the formula HF.

Association. — Many compounds resemble hydrogen fluoride in seeming to consist of molecules which are multiples of the simplest possible. This is spoken of as indicating a tendency to **association.*** Thus, sulphuric acid and nitric acid in the liquid condition are composed of more complex aggregates than H_2SO_4 and HNO_3. Even water is largely $(H_2O)_2$ or even $(H_2O)_3$, although the vapor is H_2O. In such cases *dissociation* into the simpler molecules takes place gradually as the temperature is raised. Sometimes this doubling up of molecules is called **polymerization.**

In cases of association the observed molar weights, at low temperature, are multiples of the smallest possible molar weight required for the simplest formula (in above instance, HF). But many substances naturally possess formulæ which are multiples of the simplest without showing, as the temperature is raised, any tendency to progressive dissociation into the corresponding simplest molecules. Thus, acetylene (p. 204) is C_2H_2 at all temperatures, and acetic acid (*q.v.*), although it is associated to $C_4H_8O_4$ at its boiling-point, never becomes simpler than $C_2H_4O_2$ at any temperature.

Chemical Properties of Hydrofluoric Acid. — Metals like zinc and magnesium interact with hydrofluoric acid with evolution of hydrogen. The action is less violent than with other halogen acids. The acid interacts with oxides and hydroxides, forming fluorides. The chief difference in this respect which it exhibits, when compared with the other halogen acids, is one which we should expect from its formula, H_2F_2. We may displace either one or both the hydrogen atoms in the molecule with a metal. Thus, one of the commonest salts of hydrofluoric acid is potassium hydrogen fluoride KHF_2 mentioned above, $KOH + H_2F_2 \rightarrow KHF_2 + H_2O$. In this respect the acid resembles sulphuric acid and other acids containing more than one replaceable hydrogen unit. Salts in which a portion of the acid hydrogen still remains undisplaced are spoken of as **acid salts.**

* The elementary substances show similar behavior (pp. 205, 206).

The most remarkable property of hydrofluoric acid depends on the great tendency which fluorine has to unite with silicon, forming the gaseous silicon tetrafluoride. Glass, which is commonly made by fusing together sodium carbonate, calcium oxide, and sand (silicon dioxide), is a mixture of silicates of calcium and sodium, and is rapidly decomposed by hydrofluoric acid. The nature of the change is shown by the two following equations:

$$CaSiO_3 + 3H_2F_2 \rightarrow SiF_4 + CaF_2 + 3H_2O,$$
$$Na_2SiO_3 + 3H_2F_2 \rightarrow SiF_4 + 2NaF + 3H_2O.$$

All other silicates are decomposed according to the same plan. The silicon tetrafluoride passes off. The fluorides of calcium and sodium are solid and crumble away or dissolve. Thus the glass is completely disintegrated. The vapor of hydrofluoric acid, generated in the way described above from calcium fluoride in a lead dish, is used for etching glass. The surface of the glass is covered with paraffin to protect it from the action of the vapor, and with a sharp instrument portions of this paraffin are removed where the etching effect is desired. The vapor gives a rough surface where it encounters the glass. The aqueous solution, which may also be employed, makes smooth depressions on the surface. The acid is also used in the analysis of minerals containing silicates, which frequently are not attacked by other acids.

The Halogens as a Family.

It may be useful here to bring together some of the facts in regard to the halogens and their compounds by way of showing more clearly how far they resemble one another, and in what ways they differ. The most noticeable fact is that, if we **arrange them in order in respect to any one property** chemical or physical, **the other properties will** be found to **place them in the same order.** Thus, if we consider (1) the physical properties, we find that the color deepens as we pass from fluorine through chlorine and bromine to iodine. The specific gravities of the elements increase in the same order. The volatility of the elements decreases in the same way — fluorine being the hardest to liquefy, while iodine is a solid and boils at a fairly high temperature. (2) In their chemical behavior, when, for example, they unite with the metals and hydrogen, the vigor of the action is greatest with fluorine and diminishes progressively until we reach iodine. We shall see later that the affinity for oxygen, on the other hand, *increases* as we pass from fluorine to iodine.

(3) The relations of these elements in combination show that they are all univalent in respect to union with hydrogen and metals. In their oxygen compounds (*q.v.*), however, they frequently exhibit a higher valence. The compounds which they form with any one element are usually very similar to one another. All the hydrogen compounds, for example, become acids when dissolved in water. The most noticeable lack of harmony in this group is observed when we consider the solubilities of the corresponding compounds. Thus, the potassium salts are all soluble in water. Silver chloride, bromide, and iodide are almost insoluble, the amount dissolved decreasing in that order. Silver fluoride, however, is quite soluble. Calcium chloride, bromide, and iodide are all very soluble, while calcium fluoride is almost completely insoluble.

It will be noted that the order in which the elements are thus placed by consideration of most of their properties is the order of increasing atomic weights (see Periodic system).

Compounds of the Halogens with Each Other.

We have incidentally mentioned the fact that iodine unites with chlorine to form a definite compound. In reality there are two such compounds. The most familiar is a red crystalline substance having the composition ICl. Another compound, ICl_3, is made by the use of excess of chlorine. Iodine unites with bromine to form the compound IBr, while a compound with fluorine, to which the composition IF_5 has been assigned, is supposed to exist. None of these compounds are particularly stable, and some of them decompose very easily. It is frequently stated that elements which resemble one another chemically show little tendency to chemical union. Yet in the case of IBr, for example, the tendency to decompose into the elements ($2IBr \rightarrow I_2 + Br_2$) must be interpreted as meaning that the iodine and bromine prefer to unite with themselves to form the molecules I_2 and Br_2 rather than with one another. In view of this the above remark loses some of its point, for an element certainly resembles itself more than it does any other, and the compounds Cl_2, H_2, etc., are amongst the most stable that we know.

Exercises. — 1. What impurities is commercial iodine likely to contain? In what way does heating with potassium iodide (p. 234) free it from these?

*2. Classify all the chemical actions in this chapter according as they belong to one or other of the ten kinds (p. 187).

3. Explain the condensation of atmospheric moisture by the hydrogen halides (*cf.* p. 162).

4. Tabulate, more fully and specifically than is done in the section on "The Halogens as a Family," (*a*) the physical properties, (*b*) the chemical properties, (*c*) the chemical relations, of the members of this group.

5. Construct the equation on p. 234 by the use of partial equations as in the example on p. 229.

6. Using the method given on p. 229, construct a single equation for the formation of iodine, water, and hydrogen sulphide directly from potassium iodide and sulphuric acid.

CHAPTER XV

CHEMICAL EQUILIBRIUM

In spite of its formidable title, this chapter will introduce nothing novel. Its purpose is to collect together and organize more definitely a number of scattered facts and ideas which have already come up in various connections. On this account, however, it will be all the more necessary for the reader to refresh his remembrance of these facts and ideas by re-reading the pages to which reference may be made.

Reversible Actions. — In discussing the union of hydrogen and iodine (p. 237), it was stated that the progress of the action ceases while yet a large amount of *both* the substances necessary for its maintenance still remains available. Now the materials left over are presumably no less capable of uniting than the parts which have already united. The solution of this mystery lies in the fact (p. 239) that *decomposition of the compound* can begin at 180°, and therefore takes place actively at 448°. Hence the product of the union must begin to dissociate, in part at least, as soon as any of it is formed. Thus two changes, one of which undoes the work of the other, must go on simultaneously. In consequence of this, neither can reach completion. As we should expect, experiment shows that it makes no difference whether we start with the elements or with the compound: the proportions of the materials found in the tube, after it has been heated for a sufficient length of time, are in both cases the same. A general statement may be founded on facts like this, to the effect that a chemical action must remain more or less incomplete when the reverse action also takes place under the same conditions (*cf.* p. 35). Two arrows pointing in opposite directions are used in equations representing reversible changes: *

$$H_2 + I_2 \rightleftarrows 2HI \text{ or } 2HI \rightleftarrows H_2 + I_2.$$

It will be observed that representing reversible actions by equations involves a departure from the original meaning of an equation. Thus at 448°, 80 per cent

* The reader must avoid the idea that a reversible action is one which goes to completion, and then runs back to a certain extent. This conception would be contrary to the fact, and opposed to the principles of energetics, as well as inexplicable by the kinetic hypothesis.

of the substances are in the form HI and 20 per cent in the uncombined state:

$$(80\%)\ 2HI \rightleftarrows H_2 + I_2\ (20\%).$$

In other words, the amounts of matter on the two sides are *not equal*. Each side, taken separately, shows correctly the *proportions* used in the interaction for which it stands, however. Hence the equation in a reversible action professes to show quantitatively the change which *would occur* if each of the two opposed actions it includes were to be allowed separately to proceed to completion.

The following are some other examples of actions of the same kind: (1) The interactions of sulphuric acid and sodium chloride (p. 179), and (2) of chlorine and water (p. 176), which were fully discussed at the time; (3) that of equivalent amounts of iron and water, or of magnetic oxide of iron and hydrogen (p. 110), which does not proceed to completion in either direction when either set of materials is sealed up in a tube and heated; (4) the behavior of barium peroxide (p. 63), of hydrates (p. 120), of iodine vapor (p. 205), of water vapor (p. 119), of sulphur vapor (p. 205), of phosphorus vapor (p. 205), and of mercuric oxide (pp. 62, 77).

When the action is one which is reversible, but, under the circumstances being discussed, proceeds far towards completion in one direction, the arrow will be modified to indicate this fact:

$$Cl_2 + H_2O \leftrightarrows HCl + HClO \text{ (p. 176).}$$

When this relative completeness is due to precipitation or volatilization, the fact will be indicated by vertical arrows:

$$NaCl + H_2SO_4 \leftrightarrows NaHSO_4 + HCl \uparrow \text{ (p. 178).}$$
$$NaCl \downarrow + H_2SO_4 \leftrightarrows NaHSO_4 + HCl \text{ (p. 179).}$$

All chemical actions do not belong to this class. Many proceed uninterruptedly to exhaustion of one, or all, of the ingredients. For example, equivalent amounts of magnesium and oxygen combine completely ($2Mg + O_2 \rightarrow 2MgO$). Here, however, the product is not decomposed even at the white heat produced by the vigor of the union. Indeed, magnesium oxide cannot be decomposed, and the action reversed, at any temperature we can command. The other complete actions are so because they are likewise irreversible.

Chemists now look upon reversibility as being the normal property of all chemical changes. They consider the lack of obvious incompleteness as being due to the very small degree to which the reverse action can occur under the given conditions, rather than to the entire absence of any reverse action.

Kinetic Explanation.— Restating these facts in terms of the kinetic hypothesis will enable us to reason more clearly about this

variety of chemical change. Suppose we start with the materials represented on one side of such an equation. The molecules of these materials will encounter one another frequently in the course of their movements. In a certain proportion of these collisions the chemical change will take place. In the earliest stages there will be few of the new kind of molecules, but, as the action goes on, these will increase in quantity. There will be two consequences of this. In the first place the parent materials will diminish in amount, the collisions between their molecules will become fewer, and the speed of the forward action will therefore become less and less. In the second place the increase in the number of molecules of the products will result in more frequent collisions between them, in more frequent occurrence of the chemical change which they can undergo, and thus in an increase in the speed of the reverse action. The forward action decreases in speed progressively; the reverse action increases in speed. Finally the two speeds must become equal, and at that point perceptible change in the condition of the whole must cease.

The most immediate inference from this mode of viewing the matter is, that the apparent halt in the progress of the action does not indicate any cessation of either chemical change. Both changes must go on in consequence of the continued encounter of the proper molecules. But since they proceed with equal speed they produce no alteration in the mass as a whole. In fact, the final state is one of equilibrium, and not of repose. Hence, chemical changes which are reversible lead to that condition of seemingly suspended action which we speak of as **chemical equilibrium**. The changes themselves are called **reversible**, or, since they represent a state of balance between opposing tendencies, **balanced actions**.

The detailed discussion of the relations of liquid and vapor (pp. 117, 135), of ice and water (p. 115), and of saturated solution and undissolved solid (pp. 152, 160), liquid or gas (p. 154), has already familiarized us with this term and its significance. By the use of the kinetic hypothesis we can, in fact, apply the very same sets of ideas to the discussion of any kind of reversible phenomena.

When this is done for reversible chemical actions we perceive that two circumstances, in particular, are likely to have a noteworthy effect in the promotion or retardation of a given chemical change. These are the homogeneity, or the reverse, of the mixture, and the molecular concentration of each component.

The Influence of Homogeneous Mixture. — Evidently the interaction of substances will be greatly favored if they are capable of remaining intimately mixed. When this is the case, as in gaseous or liquid mixtures, every molecule has an equal opportunity freely to encounter every other molecule. On the other hand, when one substance is a liquid and the other a gas not especially soluble in the liquid, or when one is a liquid and the other a solid suspended, but not dissolved, in the liquid, or when they are solid and gas respectively, the chances for mutual encounters between the two different kinds of molecules will be very notably restricted. Thus the progress of an action between inhomogeneously mixed bodies, otherwise capable of interaction, must be greatly affected by purely physical circumstances. Some of the remarkable consequences of this were discussed fully in connection with the preparation of hydrogen chloride (p. 179).

The Influence of Molecular Concentration. — Even when the mixture is homogeneous, a second factor will affect the action. The frequency of the encounters amongst a given set of molecules, resulting in a definite chemical change, will evidently depend entirely upon the degree to which they are concentrated in each other's neighborhood. Larger amounts of one of the materials, for example, will not result in more rapid chemical action in the sense which this material favors, if the larger amount of material is also scattered through a larger space. Chemical changes of this kind, therefore, are not accelerated by increasing the mere quantity of any ingredient, but only by increasing the **concentration of its molecules**. Hence, in practice, we find that the distribution of the molecules in a system which has reached a state of equilibrium is at once affected if we alter the molecular concentration of any of its components. Thus, if, in the action of hydrogen upon iodine, we introduce *into the same space* an extra amount of hydrogen, this facilitates the formation of hydrogen iodide by increasing the possibilities of encounter between hydrogen and iodine, while at the same time it does not affect (*cf.* p. 88) the number of encounters in a given time between hydrogen iodide molecules which result in the reverse transformation. The proportion of hydrogen iodide formed, therefore, from a given amount of iodine will be greater, although the potential maximum has not been altered since the quantity of one ingredient only has been increased. The introduction of an excess of iodine would have had precisely the same effect.

It is easy to illustrate this experimentally. If ferric chloride and ammonium thiocyanate are mixed in aqueous solution, a liquid containing the soluble, *blood-red* ferric thiocyanate is produced; $FeCl_3 + 3NH_4CNS \rightleftarrows Fe(CNS)_3 + 3NH_4Cl$. The action is a reversible one. Now, if the two just-named salts are mixed in very dilute solution in the proportions required by the equation, say by adding 20 c.c. of a deci-normal solution (p. 149) of each to several liters of water, a pale-reddish solution is obtained. When this is divided into four parts, and one is kept for reference, the addition of a little of a concentrated solution of ferric chloride to one jar, and of ammonium thiocyanate to another, will be found to deepen the color by producing more of the ferric thiocyanate. On the other hand, mixing a few drops of concentrated ammonium chloride solution with the fourth portion will be found to remove the color almost entirely on account of its influence in accelerating the backward change.

We may state (see below) as a **general principle** that, in reversible actions between substances in homogeneous mixture, the **amount of a chemical change taking place in a given time will be dependent upon the molecular concentration of each ingredient**. It will also naturally depend upon **the intrinsic affinity** (*cf.* p. 111). It will likewise **vary with the temperature**, since the affinity is affected by change in temperature.

The phrase "active mass" is sometimes employed instead of the words "molecular concentration." It is somewhat misleading, however, for, as we have seen, it is not on the mass of a substance, but on the quantity of it in a given volume, that the speed of the action depends.

Law Connecting Molecular Concentration and Speed of Reaction. — These principles must now be stated in somewhat more precise terms. We confine our attention to homogeneous mixtures, in the first place, and to non-reversible actions.

The concentration of the molecules is usually expressed, for each substance, in terms of the number (whole or fractional) of *moles* (gram-molecular weights, p. 197) of the substance contained in a liter of the whole mixture. There is the same number of molecules in a mole of every substance, namely, the number of molecules in 32 g. of oxygen (*cf.* p. 199). Hence the number of moles per liter defines the concentration of the substance in terms of this number of molecules in a liter as the unit of concentration.

Thus, in a solution containing 25.4 g. of free iodine ($\frac{1}{10}$ of a formula

weight, I_2) per liter, the solution is 0.1 molar (p. 149), and the molecular concentration of the iodine is 0.1. When the substance is a gas, the concentration of the molecules is proportional to the partial pressure of the gas. Now, one mole of a gas occupies 22.4 liters at one atmosphere pressure (and 0°). Hence, when one mole of a gas is contained in 1 liter, and its molecular concentration is therefore 1, it exercises 22.4 atmospheres partial pressure. When the partial pressure of one gas in a mixture is two atmospheres, its molecular concentration is $\frac{2}{22.4}$ or 0.09.

In an action of the form $A + B \rightarrow C + D$, let c_1 and c_2 represent the number of moles per liter of the materials A and B, respectively, at any stage of the interaction. Then the speed (S) of the forward action, expressed in moles of A and B transformed per unit of time (say, per hour), is found to be defined by the relation $c_1 \times c_2 \times F = S$. Of course c_1 and c_2 (and therefore, also, S) diminish steadily, for the materials A and B are being progressively used up. S, therefore, at any moment is the amount which would be transformed if the concentrations present at that moment were artificially maintained during the whole hour. F expresses the intrinsic activity (affinity) propelling the action, which is independent of concentration. If unit concentrations are taken, $c_1 = c_2 = 1$, and therefore $F = S$. Thus F, the activity, is always represented numerically by the speed in moles per unit of time when the concentration of each ingredient is unity. For rapid actions a shorter unit of time than the hour may be used.

In practice the value of F for any action can easily be determined, because c_1, c_2, and S can be measured. As a check on the results, different concentrations will be used at the same temperature, and the amounts transformed in measured times will be observed in each case. We can then calculate from the data of each set the speed (moles transformed per hour or minute) which would be shown by constantly maintained unit concentrations of the materials. The answers are the values of F based upon different concentrations of the same substances, and they agree closely with one another. The values of F for several different chemical actions, however, may differ widely, and are measures of the relative activity of each.

If the action is more complex, the same principles apply. Thus, if an expression for the speed of the action $2A + 3B + C \rightarrow D + E$ is required, we must consider this equivalent to $A + A + B + B + B + C \rightarrow D + E$. Here the speed forwards (S) $= c_1 \times c_1 \times c_2 \times c_2 \times c_2 \times c_3 \times F$, or $c_1^2 c_2^3 c_3 F = S$.

It need hardly be added that, clearly, when the concentration of any ingredient

becomes zero (say by all of it entering into combination), or when the affinity is zero, the speed S must become zero, that is to say, no action takes place.

The relation of the theoretical speed with constant concentration, used in the above formulæ, to that which is *observed* with diminishing concentration is rather complex. For an action of the form $A \rightarrow B + C$, where the change in only one molecule constitutes the action, if c_1 is the initial molecular concentration of A, and x is the fraction of this which is transformed in the time t,

$$S = \log_e \frac{c_1}{c_1 - x} \div t.$$

When two molecules have to interact, the formula is still more complex. If the substances are present in equivalent proportions, their molecular concentrations in this special case are alike, and may each be represented by c_1. The relation is then:

$$S = \frac{x}{c_1 (c_1 - x)} \div t.$$

The mathematical derivation of these relations will be found in any work on physical chemistry.

The **law of molecular concentration** is, therefore: **In every chemical experiment, the speed of the action at any moment is proportional to the first, or some higher power of the molar concentration, for the time being, of each interacting substance, and to the affinity at work.**

The following illustration (see also Sulphurous acid) will make all this clearer. When arsine AsH_3 (*q.v.*) is heated at 310°, it decomposes gradually into hydrogen and arsenic:

$$\underset{c_1}{AsH_3} \rightarrow As + 1\tfrac{1}{2}H_2.*$$

The action is not appreciably reversible. The arsenic assumes the solid form. The gas is inclosed in a tube which is kept in a bath at 310°, and a manometer shows changes in pressure. Since, as the action proceeds, $1\frac{1}{2}$ molecules of hydrogen take the place of each molecule of arsine, the total pressure slowly increases. Every increase of 1 mm. in the pressure is the result, therefore, of an addition of 3 mm. partial pressure of hydrogen and a reduction of 2 mm. in the partial pressure

* Ordinarily we should write the equation $2AsH_3 \rightarrow 2As + 3H_2$. But this form would make the speed proportional to c_1^2, and calculation then gives us inconstant values for S. The reason for this irregularity is given in works on physical chemistry.

of the arsine. The molecular concentrations are proportional to the pressures, and change, therefore, in the same ratios. The observations (first two columns), together with the data deduced from the first two by calculation, were as follows :

TIME, HOURS.	PRESS., MM.	MOLECULAR CONCENTRATIONS.		S. PER HOUR.
		Total.	AsH_3 Transfmd.	
0	784.84	0.02159 (c_1)	. . .	. . .
3	878.50	0.02416	0.00514	0.0906
4	904.05	. . . .	. . .	. . .
8	987.19	. . . .	. . .	. . .

We must first ascertain the molecular concentration of the arsine corresponding to the observed pressure at the beginning. We remember that at 22.4 atmospheres, or 22.4 × 760 mm. and 0°, the concentration of a gas has the value 1 (p. 251). The actual initial pressure 784.84 mm. at 310° would become, at 0°, $\frac{784.84 \times 273}{(310 + 273)}$, or 367.5 mm. The molecular concentration is here, therefore, $\frac{367.5}{22.4 \times 760}$ or 0.02159 moles per liter. After 3 hours, some hydrogen has been formed. The pressure has increased to 878.50 mm. Reducing as before, this represents a molecular concentration of all ingredients of 0.02416 moles per liter. The increase is 0.00257. This, as was demonstrated above, corresponds to a loss of 2 × 0.00257, or 0.00514 moles per liter of arsine. Now, employing the formula given above, we find the speed per hour:

$$S = \log_e \frac{c_1}{c_1 - x} \div t = \log_e \frac{0.02159}{0.01645} \div 3 = 0.0906.$$

This result means that, if the concentration of the arsine were to be maintained at the initial value by continual renewal of the waste, then 0.0906 (9.06 per cent) of the initial amount would be decomposed in an hour. Using the pressures at 4 and at 8 hours, the reader will obtain by calculation, practically the same value for S. Other experiments with still different concentrations, provided the temperature was the same (p. 250), would likewise give the same result. Hence, when we take unit concentration (1 mole per liter), $c = 1$, and the expression $c_1F = S$ becomes $F = 0.0906$. Thus the affinity or activity

of the action may be measured with any concentration, and expressed in moles transformed per hour with unit concentration. Similar measurements with other actions then enable comparisons of their relative activities to be made (see Exercise 9, end of this chapter).

The Condition for Chemical Equilibrium. — Let us now take a reversible action,

$$\underset{c_1}{A} \rightleftarrows \underset{c_2}{B} + \underset{c_3}{C},$$

in which c_1, c_2, c_3 are the molecular concentrations *after the condition of equilibrium has been established.* The above mathematical form of statement for the influence of concentration and affinity on speed of transformation, being true for all concentrations, will be true for this set. The speed of the forward and reverse actions will be,

$$S_1 = c_1F_1 \quad \text{and} \quad S_2 = c_2c_3F_2,$$

respectively, where F_1 is the intrinsic tendency of A to decompose, and F_2 the tendency of B and C to combine. As the concentrations have so adjusted themselves that an equal amount of material is being transformed each way, we have

$$c_1F_1 = c_2c_3F_2 \quad \text{or} \quad \frac{F_1}{F_2} = \frac{c_2c_3}{c_1}.$$

$\frac{F_1}{F_2}$, being the ratio of two constants, is constant ($= k$). This is the ratio of the affinities driving the opposed actions, and is known as the **affinity constant** of the reversible chemical change. If, for example, its value is $\frac{1}{4}$, then the speeds of the two actions, if each were to proceed unimpeded (say in separate vessels) with constantly maintained unit concentrations of the materials, would be in the ratio $F_1 : F_2$ or 1 : 4. From this it will be seen that measurement of the concentrations present in a system which has reached equilibrium gives us the data for calculating the value of this ratio. In other words, it gives us the means of ascertaining the relative magnitudes of the intrinsic affinities of the opposed actions.

We may apply this to the data given (p. 237) for hydrogen iodide. The equation is

$$\underset{c_1}{2HI} \rightleftarrows \underset{c_2}{H_2} + \underset{c_3}{I_2},$$

and c_1, c_2, and c_3 are the molecular concentrations after the system has come to rest. The speed of the forward action (S_1) is $c_1^2F_1$ and that of the reverse action (S_2) is $c_2c_3F_2$. As concentrations are now such that the speeds are equal, we have

$$c_1^2F_1 = c_2c_3F_2 \quad \text{or} \quad \frac{F_1}{F_2} = \frac{c_2c_3}{c_1^2} = k.$$

Now, at 448°, with equivalent quantities of the two elements, nearly 0.8 (more exactly, 79 per cent) of the weight of each is in the form HI, and 0.2 in the mixture $H_2 + I_2$. Thus in every 100 molecules, 80 are $HI(c_1)$, 10 are $H_2(c_2)$, and 10 are $I_2(c_3)$. Thus $k = 0.1^2 \div 0.8^2 = \frac{1}{64}$. That is to say, the union of hydrogen and iodine would take place with 64 times as great a speed as the dissociation of hydrogen iodide if each action could proceed without reversal and under identical conditions. Or, in terms of the kinetic theory, the collisions of the H_2 and I_2 molecules result many times more often in chemical change than do collisions of HI molecules.

The case of hydrogen iodide is comparatively simple because the volume is not altered by the progress of the action (see below). The expansion when phosphorus pentachloride (p. 208) dissociates compels us to take account of the volume. The equation is:

$$\underset{c_1}{PCl_5} \rightleftarrows \underset{c_2}{PCl_3} + \underset{c_3}{Cl_2}, \text{ and } \frac{F_1}{F_2} = k = \frac{c_2c_3}{c_1}.$$

If one gram molecule of the substance is taken, and x is the proportion dissociated, and v the volume occupied by the whole, then $c_2 = c_3 = \frac{x}{v}$ and $c_1 = \frac{1-x}{v}$. Thus $k = \frac{x^2}{(1-x)v}$. Now at 250° (and 760 mm.), for example, 0.8 of the whole weight of material is dissociated : $x = 0.8$, $1 - x = 0.2$. Hence $k = 0.8^2 \div 0.2v = 3.2 \div v$. To obtain the value of v we note that a gram molecule at 760 mm. and 0° occupies 22.4 liters. At 250° it occupies $22.4 \times (250 + 273) \div 273$ l. But *this* mass of gas contains 0.8 more molecules because of dissociation, and its volume is, therefore, $1.8 \times 22.4\,(250 + 273) \div 273 = v = 77.2$ l. Thus $k = 3.2 \div 77.2 = \frac{1}{25}$. Otherwise stated, $25\,F_1 = F_2$. That is to say, the union of the trichloride and chlorine would proceed twenty-five times as fast as the dissociation, if each of the three substances was present in unit concentration, and each action could proceed independently without reversal.

The Effect of Changes of Volume on Chemical Equilibrium. — Our applications of the theory of equilibrium will be chiefly to dissolved bodies, and hence the effect on the equilibrium point of changes in volume (by dilution or the reverse) will require frequent consideration. Now dilution, for example, diminishes opportunities for encounters between the substances on both sides of the equation. In the first of the above illustrations, increasing the volume decreases the rate at which the chlorine and the trichloride can combine. Since, however, the speed of the dissociation depends on the state of the PCl_5 molecules only, and is unaffected by their nearness to or remoteness from one another, the forward action will not be weakened at all.

Hence, dilution increases the degree of dissociation. In general, change in volume will affect the equilibrium point whenever there are more molecules on one side of the equation than on the other.

In mathematical terms, when we change the volume to $\frac{1}{n}$ times its former value (n whole or fractional), the concentration changes n times. The equation for equilibrium then becomes, momentarily, $nc_2 \times nc_3 \div nc_1 \neq k$, or $nc_2c_3 \div c_1 \neq k$. To restore the value of the expression to equality with k, change must occur in the concentrations c_2, c_3, and c_1. When n is < 1, that is, when the volume increases, some PCl_5 must pass into the form PCl_3 and Cl_2 until $c_2'c_3' \div c_1' = k$, as before. That is, dilution increases the degree of dissociation.

In the case of hydrogen iodide, and in all others where the number of molecules taking part in the direct and reverse actions *is the same*, change in the volume of the system has no effect on the position of the equilibrium point. Thus dilution diminishes the chance of encounter between two HI molecules to the same extent that it interferes with encounters between H_2 and I_2 molecules. Conversely, increase in all concentrations, by diminution of volume, favors both actions equally. Hence, at 448°, 79 per cent of HI will always be present at last, whatever the volume occupied by a given amount of the materials. In mathematical terms, if we diminish the volume n times (n whole or fractional), we increase the concentration of each constituent n times. The values become nc_1, nc_2, and nc_3 respectively,

and
$$k = \frac{n^2c_2c_3}{n^2c_1^2} = \frac{c_2c_3}{c_1^2}.$$

Heterogeneous Equilibrium. — A modification of the above conceptions is necessary when the mixture is not homogeneous. If, for example, one of the constituents is present as a solid or a gas, in greater amount than can be dissolved by the liquid in which alone the chemical change takes place, then, according to the definition of saturated solution (p. 158), the concentration of the dissolved material will be constant at a given temperature as long as physical equilibrium between the solid and the solution is maintained. This is a case especially likely to occur when slightly soluble (so-called "insoluble") bodies (*cf.* p. 146) are concerned.

The same reasoning applies also to very slightly volatile solids. The concentration of the vapor of a solid body present in excess (measured by its vapor pressure) will be constant so long as the temperature is fixed, and interaction with a superincumbent gas will take place chiefly through the vapor.

In both these cases the concentrations of the active parts of the

slightly soluble and slightly volatile bodies, respectively, are not subject to variation — they are constant. Thus, with the action,

$$\underset{c_1}{2BaO_2} \rightleftarrows \underset{c_2}{2BaO} + \underset{c_3,}{O_2,}$$

the concentrations of the vapor of $BaO_2(c_1)$ and of $BaO(c_2)$ are constant, and that of oxygen (c_3) alone is subject to alteration. We have, therefore,

$$\frac{c_2 c_3}{c_1} = k, \text{ or } c_3 = \frac{c_1}{c_2} k,$$

in which, since c_1, c_2, and k are constant, c_3 must be constant also. But the pressure of a gas is proportional to its molecular concentration, according to Avogadro's hypothesis. Therefore, in this action, the pressure of the oxygen (the **dissociation pressure**) should be constant irrespective of the extent to which the dissociation has progressed. Observation shows that this is the case. When barium dioxide is maintained at a definite temperature, the pressure of the oxygen rises to a fixed value and remains constant. Any pressure of oxygen above the fixed value forces the gas into combination until no barium monoxide is left; any pressure below this value permits the dioxide to decompose until none remains. This explains the Brin method of making oxygen (p. 63), in which a temperature is chosen at which the dissociation pressure is approximately equal to that of the partial pressure of oxygen in the air ($\frac{1}{5}$ atmosphere). All hydrates, as we have seen (pp. 121–123), behave in a precisely similar way, and furnish numberless confirmations of this application of the law of molecular concentration.

Applications in Chemistry: Displacement of Equilibria by Changes Affecting Concentration. — Of special interest to the chemist are the conditions under which the equilibrium point may be displaced and more nearly complete realization of one of the two opposed changes may be brought about.

We have just seen (p. 249) that one way in which a reversible action may be forced nearer to completion in one direction or the other is the introduction of an excess of one of the ingredients contributing to the action. This method of displacing the equilibrium point, however, cannot be very effective unless it is possible to introduce an exceedingly large excess of the selected ingredient in a high degree of molecular concentration, since this operation *does not in any way effect or, in*

particular, restrain the reverse action **which is continually undoing the** work of the forward one. A much more effective means of furthering such actions is found in *removing one of the components of the system.* Any agency which could remove the free iodine as fast as it was formed in the decomposition of hydrogen iodide, for example, would entirely stop the reproduction of the compound and so would enable the dissociation ($2HI \rightleftarrows H_2 + I_2$) to run to completion.

This might be realized * by causing one end of a sealed tube charged with hydrogen and iodine, after the contents had settled down to a condition of equilibrium, to project from the bath in which the whole had been kept at 448° (Fig. 72, which is simply diagrammatic). By cooling this end, a large part of the 21 per cent of free iodine would quickly be condensed in it to the solid form, while the hydrogen would remain gaseous. Only the trace of vapor which cold iodine gives would then be available to interact with the hydrogen and reproduce hydrogen iodide. Meanwhile the decomposition of the latter would go on, and thus, eventually, almost all the iodine would be found free in one end of the tube, and the hydrogen, all free likewise, would occupy the rest. By this purely mechanical adjustment the chemical change would in this way be carried from 21 per cent completion to almost absolute completion.

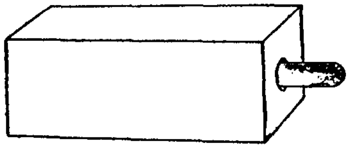


FIG. 72.

If, on the other hand, arrangements were made to have powdered marble, in a sealed bulb of thin glass, inclosed in the tube, we might imagine the very opposite effect of the above to be produced. The breaking of the bulb of marble, when equilibrium had been reached, would provide means for the removal of all the hydrogen iodide,† while the hydrogen and iodine would still be gaseous. Thus, the compound having been removed, there would be no reverse action to compensate for the union of the elements. The whole material would, therefore, soon have passed through the form HI. Hence, by another

* For another illustration, see under Ammonia.

† The hydrogen iodide would be destroyed by interaction with the marble:

$$2HI + CaCO_3 \rightarrow CaI_2 + CO_2 + H_2O.$$

The calcium iodide is a solid. The two gases, carbon dioxide and water vapor, do not interact with hydrogen or with iodine, and would not, therefore, interfere with the formation of fresh hydrogen iodide.

mechanical arrangement, an action which ordinarily could progress to only 79 per cent would be turned into a complete one.

In every-day chemical work, since our object is usually to prepare some one substance, chemists either avoid chemical changes which are notably reversible, or adjust the conditions so that the reverse of the action which they desire is prevented. In consequence of this, when carrying out the directions for making familiar preparations, the fact that such actions are reversible at all very readily escapes our notice. Arranging the conditions so that the separation of a solid body by precipitation, or the liberation of a gas, takes place, are the two commonest ways of rendering a reversible action complete. Excellent examples of both of these are furnished by the chemical change used in producing hydrogen chloride by the interaction of salt and sulphuric acid (p. 179), the discussion of which should once more be studied attentively.

The escape of one member of a system engaged in chemical interaction, because it is gaseous or solid, and in either case immiscible with the rest of the members of the system, is the commonest cause of the obstruction of one direction of a reversible action and the triumph of the other. This, as we have seen, is the combined result of the natural behavior of a system in chemical equilibrium, and of the physical properties, particularly the solubility, of the members of the system. Two rules, attributed to Berthollet, have been made, however, to describe these special cases of a broader principle. Unfortunately, it is difficult so to word them that they shall be entirely unambiguous and entirely correct.

The "rule of precipitation," for example, might read: When certain classes of materials are brought together in solution, if an exchange of radicals would produce an insoluble body, this exchange will occur. But then the fact is that, in such cases, the exchange always occurs to some extent whether any product is insoluble or not. The insolubility is responsible only for the greater completeness of the exchange. Crude statements to the effect that "when an insoluble body can be formed, it will be formed," when close scrutiny shows them to possess any definite meaning whatever, are grossly misleading. They suggest that insolubility is a sort of especially desirable career on which the elements are ambitious of entering.

All forms of these so-called laws are objectionable, because they necessarily suggest that the positive direction of the action is assisted by the immiscibility of the product, and this is the precise converse of the fact. The immiscibility does nothing at all towards assisting the formation of the insoluble substance itself, but does whatever it can towards preventing the destruction of that substance, once it is formed, by hampering the negative action.

Affinity vs. Solubility. — The question of the relation of affinity to the apparently much greater efficiency of one of the directions of some reversible actions, may now be put in a much clearer light (pp.

181, 110, and this Chap.). The whole of the possibilities of progress for any action are expressed by a function (p. 251) of the form $c_1c_2F = S$. If *any one* of the variables, say one of the concentrations (c_1), is negligible, the product must be small, irrespective of the values of the other factors. Thus the feebleness of a chemical action only shows that the product of all the variables is minute, and not that the affinity factor *per se* is of small magnitude.

Displacement of Equilibria by Changes in Temperature: Van't Hoff's Law and Le Chatelier's Law. — Since the affinities driving the two opposed actions are differently affected by change in temperature, the value of their ratio alters, and the equilibrium point, which depends on this ratio, suffers displacement. It is found that the direction of the displacement depends on which of the two actions absorbs heat, and which gives it out. In a system which is in equilibrium, **of the two opposed interactions, that one which is endothermal is promoted, while that which is exothermal is resisted, by raising the temperature, and** ***vice versa.*** This is **van't Hoff's law of mobile equilibrium.** Thus the dissociation of phosphorus pentachloride (p. 208) is endothermal (p. 27), and hence becomes greater at higher temperatures. All thermal dissociations are of this kind. Again, the interaction of steam and iron (p. 110) is exothermal, and so the higher the temperature, the more conspicuous the opposite action becomes. In view of this generalization, we can understand the formation of endothermal substances of an unstable character at high temperatures. Thus, ozone (*q.v.*) is produced by electrical discharges, and cyanogen (*q.v.*) is formed in the blast-furnace.

The principle applies also to physical equilibria. Thus, as the temperature rises, a compound which gives out heat in dissolving is less soluble in a solution already almost saturated with the compound; while one which absorbs heat in dissolving is more soluble in such a solution. For example, anhydrous sodium sulphate gives out heat in dissolving (p. 165), and its solubility diminishes (p. 158) with rising temperature, while with hydrated sodium sulphate just the converse is observed. So, also, the vaporization of a liquid absorbs heat, and hence the concentration of vapor it can maintain increases with rise in temperature.

The above law is a particular case of a still more general one frequently called **Le Chatelier's law: If some stress** (for example, by change of temperature, pressure, or concentration) **is brought to bear on a system in equi-**

librium, by which the equilibrium is displaced, the equilibrium is displaced in that direction which tends to undo the effect of the stress. Thus, pressure causes ice to melt because the water which is formed occupies a smaller volume, and the change therefore tends to relieve the pressure. So, also, the production (say, by a chemical interaction) of a large amount of a body in solution, by which its concentration is increased beyond saturation, leads to crystallization (or precipitation) of the excess.

Exercises. — 1. What is the molecular concentration of the oxygen in the air (pp. 155, 250), of the nitrogen in the air, of the aqueous vapor above water at 10° and at 20° (p. 116), of a solution containing one formula-weight of sodium chloride in 10 liters, of a solution containing 65 g. of hydrogen iodide in 250 c.c.?

2. What are the partial pressures of the three components of phosphorus pentachloride vapor at 250° and 760 mm. (p. 207)? What are their molecular concentrations?

3. Using the model on p. 254, study the dissociation of KI_3 (p. 235), of iodine vapor (p. 236), and of hydrogen iodide (p. 237), and the formation of ferric thiocyanate (p. 250). Show in each case the effect on the system of increase in volume without change in the amount of material (p. 255).

4. Using the model on p. 257, study the dissociation of mercuric oxide (p. 12), assuming the compound to be involatile, and the interaction of iron and steam (p. 110). Why can magnetic oxide of iron be reduced completely by a stream of hydrogen (p. 110), and iron oxidized completely by a current of steam (p. 99)?

5. What actions in Chap. xiv are complete for the same reason that the action of sulphuric acid on salt (pp. 178–180) is so?

6. Why is the formation of the following substances complete: silver chloride (p. 186), and hydrogen chloride and water by union of the elements?

7. What inference should you draw from the fact that the solubilities of potassium nitrate, sodium chloride, and Glauber's salt (p. 157) increase with rise in temperature (p. 260), and from the fact that those of calcium citrate (p. 156) and triethylamine decrease with rise in temperature?

8. Is the heat of solution of lead nitrate (p. 157) positive or negative?

9. Carry out the calculation of S for 4 and 8 hours (p. 253).

Summary of Principles.

The summary of some of the chief principles of the science (p. 188) may now receive several important additions. For the sake of completeness, reference to the periodic system is made in No. 21, to isomers in No. 22, and to the phase rule in No. 23, although these subjects have not yet been taken up. As before, all hypothetical matters have been excluded as far as possible.

15. That weight of each *substance* which in the gaseous condition occupies the same volume as 32 grams of oxygen, temperature and pressure being alike for both (namely, 22.4 liters at 0° and 760 mm.), is taken as the chemical unit of weight for the substance, and is known as its *molar weight* (p. 199).

16. That weight of each *element* which is the greatest common measure of the quantities of the element found in the molar weights of its compounds is taken as the chemical unit of weight for the element, and is known as its *atomic weight.* This weight has the property described in 6 (p. 188).

The composition of each substance is expressed in terms of the atomic weights as units, and the sum of the atomic weights is multiplied by an integer, when necessary, so as to equal the molar weight (p. 204).

17. The number of equivalent weights of hydrogen which combine with, or are displaced by the atomic weight of an element is called the valence of the element (p. 103).

18. The speed of every interaction is a function of the first, or some higher power of the molar concentration of each interacting substance (p. 252).

19. Substances undergoing, at a fixed temperature, an interaction which is reversible, reach a condition of equilibrium. The final proportions of the materials are such that the speeds (see 18) of the opposed actions are equal (p. 254).

20. Van 't Hoff's law and Le Chatelier's law (p. 260).

21. Each *element* has its own set of chemical relations (pp. 177, 226) : *e.g.*, it can exist in combination with certain other elements; it has a certain valence, and may have more than one valence ; it confers certain properties on its compounds as a class ; it resembles certain other elements in several of these respects (*e.g.*, the halogens), and differs from others, in a way more or less definitely described by its place in the periodic system (*q.v.*).

In complex cases, the inter-relations of the elementary units in a compound, and the relations of the compound to other compounds (see No. 22), are represented graphically by formulæ based upon an hypothesis of molecular structure (p. 224).

22. Identical combinations of matter may constitute more than one compound substance (isomers, see Urea). These may have equal molar weights (optical and structural isomers), or they may have different molar weights (pp. 204, 242).

23. In a system in equilibrium the number of components plus two equals the number of phases plus the number of degrees of freedom (Phase rule, *q.v.*).

CHAPTER XVI

OXIDES AND OXYGEN ACIDS OF THE HALOGENS

THE chief subjects of practical importance touched upon in this chapter are connected with bleaching powder ($CaCl(OCl)$), and potassium chlorate ($KClO_3$) and perchlorate ($KClO_4$). Hence our attention will be largely directed to the modes of making these substances and to their relations to one another. Incidentally, we shall encounter many actions of a complex and, to us, more or less novel kind.

Compounds of Chlorine Containing Oxygen. — The following are the names and formulæ of the substances:

$HClO$ Hypochlorous acid,	Cl_2O Hypochlorous anhydride,
($HClO_2$) Chlorous acid,	. . . .
. . . .	ClO_2 Chlorine dioxide,
$HClO_3$ Chloric acid,	. . . .
$HClO_4$ Perchloric acid,	Cl_2O_7 Perchloric anhydride.

There are also compounds of metals with the negative radicals of these acids. Of this nature are the three substances mentioned in the first paragraph. Chlorous acid is itself unknown, but potassium chlorite ($KClO_2$) and some other derivatives have been made.

The two anhydrides (p. 71), when brought into contact with water, combine with it to form the acids opposite which they stand in the table. Chlorine dioxide (*q.v.*), however, is not related to any one acid in this way.

All these compounds differ from most that we have hitherto discussed inasmuch as not one of them can be made by direct union of the simple substances.

Nomenclature of Acids and Salts. — When several compounds closely related in composition, like the above acids, are known, a systematic method of naming them is used. The terminations *-ous* and *-ic* indicate smaller and larger proportions of oxygen respectively. For compounds below or above those two in their degree of oxidation, the prefixes *hypo-* and *per-* are employed.

When the radicals (p. 93) contained in the acids are combined with metals, the compounds are spoken of as **salts** of the respective acids. Thus, $KClO_3$ is described as the potassium salt of chloric acid. The specific names for these salts are distinguished by terminations corresponding to those of the acids:

$KClO$ Potassium hypochlorite,	$KClO_3$ Potassium chlorate,
$KClO_2$ Potassium chlorite,	$KClO_4$ Potassium perchlorate.

The termination *-ite* corresponds to *-ous*, *-ate* to *-ic*. This principle is applied systematically, so that the salts of sulphuric and sulphurous acids, for example, are called sulphates and sulphites respectively.

Compounds containing no oxygen receive the termination *-ide*. Thus, KCl is potassium chloride, FeS is ferrous sulphide.

Salts and Double Decomposition. — We have just been using the word *salt* in a general sense. It is the class name for a set of substances which includes common salt or sodium chloride (NaCl), potassium nitrate (KNO_3), sodium sulphate (Na_2SO_4), silver chloride (AgCl), potassium chlorate ($KClO_3$), etc. The majority of the substances used in elementary chemistry belong to this class. They receive the name because in certain important chemical respects they behave like common salt. For example, when sodium chloride is treated with acids, such as sulphuric acid (p. 178) or phosphoric acid (p. 179), hydrogen chloride is liberated. Actions of this kind consist in an exchange of radicals and are all reversible. An action of the same type, although outwardly different, is that of sodium chloride and silver nitrate in aqueous solution (p. 99). Here we have two salts interacting instead of an acid and a salt, and we get a precipitate instead of a gas. But the interchange of radicals is exactly similar.

Now **salts** in general behave in these respects in the same way as does common salt. They **interact with acids or other salts**, particularly in solution, in such a way that **an exchange of radicals takes place**. In the first case, a salt and an acid, and in the second case two salts, are produced. **These actions are all reversible.** Acids differ thus from salts only in the fact that one of their radicals is hydrogen. Hence they are frequently called hydrogen chloride, hydrogen sulphate (H_2SO_4), and so forth. It may be added that **bases** (p. 119), like potassium hydroxide (KOH), interact reversibly with salts and acids, exchanging radicals after the same fashion.

All salts are named according to the radicals which they contain.

Thus, all containing $-SO_4$ are sulphates. Conversely, when the name of a salt is given, the formula can be written down at once. In doing this, however, regard must be had to the valence of the radicals (p. 104).

In view of the reversibility of most of the interactions of salts, acids, and bases, we encounter completed changes chiefly when precipitation occurs, or when one product is volatile (p. 259). If neither of the products formed by the exchange of radicals is insoluble, the reversibility of the action prevents our obtaining anything but a mixture. Only those double decompositions which involve more or less insoluble or volatile substances are thus of use for preparing salts. The action of sodium chloride on silver nitrate (p. 99) is an example. The silver chloride is almost completely insoluble, while the sodium nitrate produced by the change remains dissolved. By filtration we obtain the silver chloride as a powder, while the evaporation of the filtrate gives us the soluble product. This sort of action can be used, therefore, **either for the preparation of a soluble or an insoluble substance.** If the problem is to make a *soluble* product, then we must arrange an action between two substances, each containing one of the two required radicals, and possessing two other radicals, which, when united, give an insoluble body. This plan is illustrated frequently in what follows.

Hypochlorites. — Since none of the acids in our list can be made directly from their elements, we generally have to prepare, first, the corresponding salt. From the salt, by double decomposition, the acid is then secured. Hence, in each case, the salts will be discussed first.

Chlorine interacts slightly with water (p. 176), producing small quantities of hydrogen chloride and hypochlorous acid (equation (1), below). The action is very strongly reversible. That is to say, since the last two substances interact very vigorously to reproduce chlorine and water, the direct action does not make much progress.

When, however, some substance which can interact with these products is added to the solution of chlorine, or when chlorine gas is simply passed into an aqueous solution of such a substance, displacement of the equilibrium point at once occurs (p. 258). Now potassium hydroxide is a suitable substance. It interacts almost completely in solution with both the products of this action, producing potassium chloride (2) and potassium hypochlorite (3), according to the last two of the following equations :

$$Cl_2 + H_2O \leftrightarrows HCl + HOCl, \qquad (1)$$
$$HCl + KOH \rightarrow KCl + H_2O, \qquad (2)$$
$$HOCl + KOH \rightarrow KOCl + H_2O.* \qquad (3)$$

Thus, omitting the water which appears both among products and initial substances, and the two acids which are used up as quickly as they are produced by the first action, we get, by addition of the three partial equations (*cf.* p. 228), the final equation :

$$Cl_2 + 2KOH \rightarrow KCl + KOCl + H_2O.$$

This sort of action does not give a pure hypochlorite, but for some purposes the presence of the chloride in the solution is not objectionable.

Bleaching powder, CaCl(OCl), is manufactured on a large scale by an action exactly like the above. The neutralization of a molecule of each of the two acids, however, can be accomplished by a *single* molecule of slaked lime (calcium hydroxide, $Ca(OH)_2$), since the latter contains *two* hydroxyl (OH) groups. The hydroxide can be applied either in the dry form or mixed with some water as a paste. The separate actions and final equation are as follows :

$$Cl_2 + H_2O \leftrightarrows HCl + HOCl \qquad (1)$$
$$Ca\begin{cases}OH + HCl\\OH + HOCl\end{cases} \rightarrow Ca\begin{cases}Cl\\OCl\end{cases} + 2H_2O \qquad (2)$$
$$\overline{Cl_2 + Ca(OH)_2 \rightarrow CaCl(OCl) + H_2O}$$

Bleaching powder (see Calcium) is a salt of calcium involving two different acids (a mixed salt). This condition, again, does not interfere with the application of the substance commercially. A method of obtaining pure hypochlorites, however, will be found below.

Hypochlorites change into chlorates (*q.v.*) when heated. They may also give off oxygen, $2CaCl(OCl) \rightarrow 2CaCl_2 + O_2$. Although this decomposition is slow in cold solutions of hypochlorites, or when they are preserved in the dry form, it may be hastened by means of catalytic agents. The addition of a little cobalt hydroxide (*q.v.*) to bleaching powder solution causes rapid evolution of oxygen. The hypochlorites are manufactured because hypochlorous acid, which is used in bleaching, can readily be made from them. The acid itself will not keep, except when largely diluted, and consequently cannot be transported conveniently.

* The interaction of potassium hydroxide, or any other base, with any acid to produce a salt and water, is called **neutralization** (*cf.* p. 186).

Preparation of Hypochlorous Acid: Hypochlorous Anhydride. — 1. The common method of obtaining the acid is by double decomposition, using some other acid (p. 264). Even from such a mixture, or mixed salt, as is produced by the action of chlorine on a base (p. 266), the acid may be obtained in fairly pure condition. Thus, with nitric acid (an active acid), we have, simultaneously, the two reversible actions:

$$\begin{cases} KOCl + HNO_3 \leftrightarrows KNO_3 + HOCl, \\ KCl + HNO_3 \rightleftarrows KNO_3 + HCl. \end{cases}$$

But hypochlorous acid is a feeble acid, while hydrochloric acid is an active one, so that in the former action the reversing tendency is very slight, while in the latter it is vigorous. Hence, by adding nitric acid, in amount barely sufficient for the liberation of the hypochlorous acid alone, and doing this in a very dilute solution, the object is attained. The potassium chloride is hardly affected. By gently warming the liquid a dilute solution of hypochlorous acid can be distilled off. The operation may be performed even more successfully by use of a weak acid, instead of an active one like nitric acid. Boric acid (*q.v.*) is suited to the purpose.

2. Advantage may be taken of the feebleness of hypochlorous acid in another way. When powdered chalk ($CaCO_3$) is added to chlorine water, or chlorine is passed into water holding chalk in suspension, only the hydrogen chloride has any appreciable action upon the chalk. It gives, by exchange of radicals, calcium chloride and carbonic acid (equation (2), below). The latter decomposes immediately with effervescence, yielding water and carbon dioxide gas (equation (3)).

In this particular example of equation-making (*cf.* p. 229) the three partial equations, in their simplest forms, may not be added together. Before this can be done we must always see that the terms which appear on both sides of the equations, *and are not actual products*, will disappear by cancellation. Here, the 2HCl in equation (2) will not cancel with the first product in equation (1), unless the whole of this equation is multiplied by two. The multiplication has therefore been effected:

$$\begin{array}{rl} 2Cl_2 + 2H_2O \leftrightarrows 2HCl + 2HOCl & (1) \\ 2HCl + CaCO_3 \leftrightarrows CaCl_2 + H_2CO_3 & (2) \\ H_2CO_3 \leftrightarrows H_2O + CO_2 & (3) \\ \hline 2Cl_2 + CaCO_3 + H_2O \rightarrow CaCl_2 + CO_2 \uparrow + 2HOCl. & \end{array}$$

This action gives a solution containing calcium chloride and hypochlorous acid, and, by distillation, as in the first method, a dilute solution of the acid may be secured.

3. The **anhydride of hypochlorous acid** (Cl_2O) may be obtained by passing chlorine gas over mercuric oxide. For this purpose precipitated mercuric oxide (*q.v.*) must be used, and it should be heated in advance in order to coarsen the grain of its particles and so diminish the speed with which it is acted upon. Each of the constituents of the oxide combines with chlorine:

$$HgO + 2Cl_2 \rightarrow HgCl_2 + Cl_2O.$$

The mercuric chloride then unites with another formula-weight of the mercuric oxide to form a compound $HgO, HgCl_2$, which remains in the tube. The chlorine monoxide is a reddish-yellow gas. It may be reduced to the liquid form, and boils at + 5°. Both the gaseous and liquefied forms of it, the former when heated, the latter when touched by paper or dust, decompose into the constituents with explosion. The gas dissolves in water very easily (200: 1, by vol.). The yellow solution of hypochlorous acid which results,

$$Cl_2O + H_2O \leftrightarrows 2HOCl,$$

has a strong odor of chlorine monoxide. The combination is reversible, and, when the liquid is warm, a little of the gas escapes.

Properties of Hypochlorous Acid. — 1. Hypochlorous acid cannot be made, excepting in solution, or kept, excepting in dilute solution. This is in consequence of its tendency to decompose in three different ways, one of which has just been mentioned (see 3 and 4 below).

2. As an acid it neutralizes (p. 266) active bases, giving hypochlorites.

3. If the solution is concentrated, much of the hypochlorous acid changes gradually into chloric acid and hydrogen chloride. This occurs even in the dark.

$$3HClO \rightarrow HClO_3 + 2HCl.$$

4. When the solution is warmed, but more especially when it is exposed to sunlight, oxygen is evolved rapidly.

$$2HOCl \rightarrow 2HCl + O_2.$$

This decomposition always takes place whether the acid is present alone in the water, or along with other substances. Hence, the solution of chlorine in water, which contains a small amount of hypochlorous acid, on being exposed to the bright sunlight gives off bubbles of oxygen in rapid succession. This decomposition, since it removes one of the interacting substances in the reverse action, $Cl_2 + H_2O \leftrightarrows HCl + HOCl$, enables the interaction of chlorine and water to go on to completion. Consequently, the final liquid contains nothing but hydrochloric acid and water. Leaving out the intermediate steps again, the action *appears*, therefore, to be simply a decomposition of water by chlorine.

$$2Cl_2 + 2H_2O \rightarrow 4HCl + O_2.$$

5. In consequence of the ease with which it gives up oxygen, hypochlorous acid is a strong oxidizing agent.

Hypochlorous Acid as an Oxidizing Agent: Bleaching.— Both iodine and bromine are oxidized by hypochlorous acid, the former much more rapidly than the latter, $2HOCl + I_2 \rightarrow 2HOI + Cl_2$. Further oxidation to HIO_3 occurs immediately. Although iodine has less affinity for *hydrogen* than has chlorine (p. 239), this action shows that the relation towards *oxygen* is just the opposite. Here the iodine goes into combination and the chlorine is displaced.

It is on account of its oxidizing power that hypochlorous acid is used commercially in **bleaching**. It is not applied to paints, which are chiefly mineral substances, but to complex compounds of carbon, such as constitute the coloring matters of plants and of those artificial dyes whose manufacture has now become so gigantic an industry. It should be understood that the great majority of the complex compounds of carbon are colorless. Even a slight chemical change, affecting only one or two of the atoms in a complex molecule, is thus almost sure to give a colorless or much less strongly colored material. Indigo ($C_{16}H_{10}N_2O_2$), which has a deep-blue color, is an example of a vegetable dye which is also made artificially. Hypochlorous acid oxidizes it to isatin, a yellow substance relatively pale in color:

$$C_{16}H_{10}N_2O_2 + 2HOCl \rightarrow 2C_8H_5NO_2 + 2HCl.$$

In ways just as definite as this, hypochlorous acid will change the composition of other colored substances, although, since we do not know the formulæ of all these substances, we cannot always write

equations for the actions. Thus, the interaction by which chlorophyll, the green coloring matter of plants, is bleached is doubtless similar to the above, although the formulæ of materials concerned are unknown.

On account of the hypochlorous acid which is already present in chlorine water, this solution is a very efficient bleaching agent. The removal of this one of the factors in the reverse action (p. 265) enables more of the acids to be produced from the chlorine and water until the whole of the former has been consumed.

As a rule, **bleaching** is actually carried out by liberating hypochlorous acid from bleaching powder by means of sulphuric acid:

$$Ca\begin{matrix} \diagup OCl \\ \diagdown Cl \end{matrix} + \begin{matrix} H\diagdown \\ H\diagup \end{matrix} SO_4 \rightarrow CaSO_4 + \left.\begin{matrix} HOCl \\ HCl \end{matrix}\right\} \leftrightarrows H_2O + Cl_2.$$

Of course, temporarily, most of the hypochlorous acid interacts with the hydrochloric acid to give chlorine and water, but, as the residual hypochlorous acid loses its oxygen, the secondary action is again displaced backwards until the chlorine is all used up.

The yarn or cloth is first cleansed from fatty or oily material by boiling with soap solution. It is then immersed in bleaching powder solution, and finally in dilute sulphuric acid. Both solutions must be very weak in order that no interaction may occur with the fabric itself. The last two processes may be repeated, if the brownish or yellowish coloring material has not disappeared after the first treatment.

Hypochlorous acid can be used to bleach linen or cotton, because the body of these materials, apart from the small amount of coloring matter, is composed of compounds containing nothing but carbon, hydrogen, and oxygen. These compounds are very slowly affected by hypochlorous acid, unless too strong a solution is used, or the exposure to its influence is too long. That chemical interaction does occur is shown by the "rotting" of goods which have not been washed thoroughly after bleaching. Wool, silk, and feathers, on the other hand, are composed largely of compounds containing nitrogen in addition to the above three elements. Their constituent material interacts as easily with hypochlorous acid as do the traces of coloring substances. Hence, since the fabric itself would be attacked by this agent, different means of bleaching have to be used for materials of this class.

It should be understood that a cold dilute solution of hypochlorous

acid may be kept almost indefinitely and will not give up its oxygen spontaneously. The transfer takes place when, and only when, the acid comes in contact with some substance capable of uniting with oxygen.

Thermochemistry of Hypochlorous Acid. — As we have seen (p. 27), chemical changes which proceed spontaneously to completion are accompanied by a transformation of chemical energy into some other form of energy. Hence, a substance, or system of substances, which undergoes such a change, possesses more chemical energy and activity before the change than after it. In consequence, if some given chemical change *uses* the products of such an action, and can be brought about by the employment of the original substance, the employment of the latter will involve a greater liberation of energy, and will therefore be more likely to secure the consummation of the change in question.

The decomposition of hypochlorous acid and of chlorine monoxide are cases where there is a very marked difference between the amount of chemical energy in the original substances and in the products of decomposition, hydrogen chloride and free oxygen in the first case, and free chlorine and oxygen in the second. Hence the changes into these substances sometimes are of the nature described as explosive. A more important fact, however, is that, on this account, hypochlorous acid and chlorine monoxide are more active oxidizing agents than is free oxygen gas. The energy liberated in the decomposition of the hypochlorous acid has to be *added* (p. 78) to that which free oxygen could give, if performing the same oxidation, in order that the total fall in energy, which measures the tendency of the action to take place, may be estimated. Hence, substances that are not affected by free oxygen may be changed instantly by hypochlorous acid. This explains, for example, the oxidation by hypochlorous acid of many carbon compounds, including those which are colored, when atmospheric air is without action. Thus, the heat liberated in the oxidation of indigo to isatin by oxygen gas, if it could be carried out, would be 1800 cal. The much greater heat liberated when hypochlorous acid is used, we obtain by adding the thermochemical equations:

$$2HClO = 2HCl + 2O + 18,600 \text{ cal.}$$
$$C_{16}H_{10}N_2O_2 + 2O = 2C_8H_5NO_2 + 1800 \text{ cal.}$$
$$\overline{C_{16}H_{10}N_2O_2 + 2HClO = 2C_8H_5NO_2 + 2HCl + 20,400 \text{ cal.}}$$

The following thermochemical equations give a rough idea of the relative oxidizing powers of the chief oxygen acids of the halogens :

$HClO, Aq = HCl, Aq + O + 9300$ cal.,	or + 9,300	cal. for *each* atomic weight of oxygen.
$HClO_3, Aq = HCl, Aq + 3O + 15,300$ cal.,	or + 5,100	
$HClO_4, Aq = HCl, Aq + 4O + 700$ cal.,	or + 170	
$HBrO_3, Aq = HBr, Aq + 3O + 15,000$ cal.,	or + 5,000	
$HIO_3, Aq = HI, Aq + 3O - 42,900$ cal.,	or − 14,300	
$HIO_4, Aq = HI, Aq + 4O - 34,500$ cal.,	or − 8,600	

Formerly a different explanation for actions like that of hypochlorous acid, when it behaves as an oxidizing agent, was offered. It was suggested that the oxygen was first liberated from the acid ($HOCl \rightarrow HCl + O$), and that the single *atoms* of the element so produced were more active than molecular oxygen. This oxygen, which was supposed to interact in the moment of its production, was called **nascent oxygen**. But it will be seen that such an explanation is entirely unnecessary. The activity of the hypochlorous acid on account of its large store of free energy sufficiently accounts for the facts (see Nascent hydrogen).

Simultaneous, Independent Chemical Changes in the Same Substance. — As we have seen, hypochlorous acid undergoes three different changes. Some molecules decompose into water and chlorine monoxide (p. 268), while others give chloric acid and hydrogen chloride, and still others hydrogen chloride and oxygen. Since the *same molecule* cannot undergo more than one of these different changes, it follows that the actions are independent of one another. This is shown by the fact that in sunlight the third predominates, while in the dark it falls far behind the second. Since the *relative* quantities of the products vary, the several simultaneous actions cannot be put in the same equation. The fundamental property of an equation is to show the *constant* proportions by weight between every pair of substances in it. Hence three separate equations are required in the present, and in all similar cases where all the proportions are not constant (*cf.* p. 231 and see Perchlorates). *Successive* actions, like (1) preceded by (2) in the next section (*cf.* p. 266), however, may be combined in one equation, since in them all the proportions must necessarily be constant. These equations are interlocked, for (1) consumes what (2) produces.

Chlorates. — Like hypochlorous acid itself, the hypochlorites turn into chlorates. Thus, when chlorine is passed into a warm, concentrated solution of potassium hydroxide, and particularly when an excess of chlorine is used, the hypochlorite changes into chlorate as fast as it forms :

$$3KClO \rightarrow KClO_3 + 2KCl \qquad (1)$$

To secure the three molecules of the hypochlorite, the equation formerly given (p. 266) must be tripled:

$$3Cl_2 + 6KOH \rightarrow 3KCl + 3KClO + 3H_2O. \qquad (2)$$

When these are added, and the intermediate substance is left out, the final equation is obtained:

$$3Cl_2 + 6KOH \rightarrow KClO_3 + 5KCl + 3H_2O.$$

When the solution is cooled, the chlorate crystallizes out.

This action involves converting five-sixths of the valuable potassium hydroxide into the relatively less valuable potassium chloride. Hence, in practice, the makers carry out the corresponding action with calcium hydroxide. They then add potassium chloride to the resulting solution, containing calcium chloride and calcium chlorate ($Ca(ClO_3)_2$). The potassium chlorate, formed by double decomposition, crystallizes when the solution is cooled.

All chlorates are at least moderately soluble in water. Potassium chlorate is used in making fireworks, explosives, and matches. An intimate mixture with sugar ($C_{12}H_{22}O_{11}$) burns with semi-explosive violence, the oxygen of the salt combining with the carbon and hydrogen to form carbon dioxide and water. Detonating fuses for artillery are made of a mixture of this salt with antimony trisulphide (*q.v.*).

The Separation of Substances by their Solubility. — When neither of the products of an action approaches absolute insolubility, a separation may nevertheless be effected more or less perfectly by taking advantage of difference in solubility. Thus, in the practical method of making potassium chlorate, the calcium chloride is exceedingly soluble, while the potassium chlorate is only moderately so. Then, too, the solubility of the latter decreases rapidly as the temperature is lowered (Fig. 61, p. 157). Hence, it is found that when the mixture is cooled to $-18°$ only about 13.5 g. of potassium chlorate remain dissolved in each liter, and are lost. At 0° the loss would be greater, for at this temperature a liter of pure water would hold 33.3 g., and a liter of this solution would contain more than this on account of the uncompleted reversible action (*cf.* p. 264):

$$Ca(ClO_3)_2 + 2KCl \rightleftarrows CaCl_2 + 2KClO_3.$$

It will be seen that we reason as if the solubility of each substance was independent of the presence of other dissolved bodies (p. 153).

By the use of this principle, and the data in regard to solubility in Fig. 61 (p. 157), a rough idea may be obtained of what may be expected in any given case. From the diagram the solubilities at any given temperature may be read. Suppose, for example, the question is in regard to the quantity of potassium

chlorate we may expect to obtain from 3 g. of potassium hydroxide dissolved in 7 g. of water (a 30 per cent solution). From the equation:

$$3Cl_2 + 6KOH \rightarrow KClO_3 + 5KCl + 3H_2O$$
$$\quad 6\times 56 \qquad 122.5 \qquad 5\times 74.5$$

we find that 336 g. of potassium hydroxide give 122.5 g. of chlorate and 372.5 g. of chloride. Hence, by proportion, 3 g. will give about 1 g. and 3 g. respectively. The solubility, read from the diagram, is the amount of the salt dissolved by 100 c.c. of water, for example, 56.5 g. of potassium chloride at 100°. Some of the results are given in the form of a table:

	Potassium Chloride.	Potassium Chlorate.
Amount formed from 3 g. KOH.	3.0	1.0
Solubility at 100° in 100 c.c. Aq	56.5	56.5
Solubility at 100° in 7 c.c. Aq	4.0	4.0
Solubility at 20° in 100 c.c. Aq	34.7	7.5
Solubility at 20° in 7 c.c. Aq	2.5	0.5
Solubility at 0° in 100 c.c. Aq	28.0	3.3
Solubility at 0° in 7 c.c. Aq	2.0	0.25

Thus, at 20°, at least 2.5 g. of the 3 g. of potassium chloride will remain dissolved, while half of the potassium chlorate will crystallize out. If the solubilities are examined, it will be seen that the potassium chlorate is even more easily obtainable in pure condition when calcium chloride takes the place of potassium chloride.

Chloric Acid. —This acid may be obtained in solution in water, by adding the calculated amount of diluted sulphuric acid to a solution of barium chlorate:

$$Ba(ClO_3)_2 + H_2SO_4 \rightleftarrows BaSO_4\downarrow + 2HClO_3.$$

The barium sulphate, being insoluble, is removed by filtration (*cf.* p. 265).

The solution may be concentrated (to about 40 per cent) by evaporation, but must not be heated above 40°, as the acid decomposes near this temperature. The resulting thick, colorless liquid has powerful oxidizing qualities, setting fire to paper (made of cellulose, $C_6H_{10}O_5$) which has been dipped into it. It converts iodine into iodic acid, $2HClO_3 + I_2 \rightarrow 2HIO_3 + Cl_2$. When warmed beyond 40° the acid decomposes, giving chlorine dioxide and perchloric acid (see below).

Making of Equations Once More. —The equation for the last action, although far from simple, may be made readily by use of a device

which can always be applied where *an oxygen acid gives an oxide.* The formula of the initial substance, chloric acid, may be written thus, H_2O,Cl_2O_5, so as to show the anhydride (in this case imaginary) to which it is related. Now the products are ClO_2 and perchloric acid, and the latter may be written H_2O,Cl_2O_7. Disregarding the elements of water, we perceive that some Cl_2O_5 becomes Cl_2O_7, while the rest of the Cl_2O_5 furnishes the oxygen for this change and itself falls to $2ClO_2$. Evidently one molecule undergoing the former change will require two undergoing the latter in order that it may secure the two units of oxygen :

$$2H_2O,Cl_2O_5 \rightarrow 2H_2O + 4ClO_2 (+ 2O), \qquad (1)$$

$$H_2O,Cl_2O_5 (+ 2O) \rightarrow H_2O,Cl_2O_7. \qquad (2)$$

Adding and dividing by 2, we have :

$$3HClO_3 \rightarrow H_2O + 2ClO_2 + HClO_4.$$

Chlorine Dioxide: Chlorous Acid. — Chlorine dioxide is a yellow gas which may be liquefied, and boils at + 10°. The gas and liquid are violently explosive, the substance being resolved into its elements with liberation of much heat. It is formed whenever chloric acid is set free, and hence it is seen when a little powdered potassium chlorate is touched with a drop of concentrated sulphuric acid. Concentrated hydrochloric acid turns yellow from the same cause when any chlorate is added to it. These actions are used as tests for chlorates, and distinguish them from perchlorates (*q.v.*). With water, chlorine dioxide gives a mixture of chlorous and chloric acids, and with bases a mixture of the **chlorite** and chlorate.

Perchlorates, Perchloric Acid, and Perchloric Anhydride. — When heated, chloric acid and chlorates give perchloric acid (p. 274) and perchlorates respectively. The chlorates also give oxygen at the same time (p. 64) :

$$\begin{cases} 2KClO_3 \rightarrow 2KCl + 3O_2, \\ 4KClO_3 \rightarrow 3KClO_4 + KCl. \end{cases}$$

These actions, like the three decompositions of hypochlorous acid, are independent, and proceed simultaneously (p. 272). Their relative speed, however, varies with the temperature, and the decomposition into chloride and oxygen may completely outrun the other when a

catalytic agent like manganese dioxide is added (p. 65). When pure potassium chlorate is heated cautiously, about one-fifth of it has lost all its oxygen by the time the rest has turned into perchlorate. The mixture may be separated by grinding with the minimum quantity of water which will dissolve the chloride it contains. The perchlorate, having at 15° less than one-twentieth of the solubility of the chloride, will remain, for the most part, undissolved. The perchlorates are much more stable (p. 119) than the chlorates, or hypochlorites: they are all soluble in water, and they are used in making matches and fireworks.

Pure **perchloric acid** explodes when heated above 92°. But, like other liquids, its boiling-point is lower when its vapor is under reduced pressure (p. 118). At 56 mm. pressure it boils at 39°, a temperature at which hardly any decomposition is noticeable. Hence the acid may be made by mixing potassium perchlorate and concentrated sulphuric acid and distilling the mixture cautiously in a vacuum:

$$KClO_4 + H_2SO_4 \rightleftarrows KHSO_4 + HClO_4\uparrow.$$

To secure the requisite low pressure, the ordinary distilling apparatus (Fig. 16, p. 38) is made completely air-tight, and is connected by a branch tube with a water-pump.

Perchloric acid is a colorless liquid, which decomposes, and often explodes spontaneously, when kept. A 70 per cent solution in water is perfectly stable, however. Although it is an active oxidizing agent, it is not so active as chloric acid, and does not oxidize hydrogen chloride in cold aqueous solution. When liberated by concentrated sulphuric acid it does not at once give the yellow chlorine dioxide (p. 275).

The **anhydride** (Cl_2O_7) may be prepared by adding phosphoric anhydride to perchloric acid in a vessel immersed in a freezing mixture, $P_2O_5 + 2HClO_4 \rightarrow 2HPO_3 + Cl_2O_7$. Phosphoric anhydride is often used in this way for removing the elements of water from compounds. By gently warming the mixture, the perchloric anhydride can be distilled off. It is a colorless liquid boiling at 82° (760 mm.), and exploding when struck or too strongly heated.

Oxygen Acids of Bromine. — No oxides of bromine have been made, but the acids HBrO (hypobromous acid) and $HBrO_3$ (bromic acid) and their salts are familiar.

By the action of bromine on dilute, cold potassium hydroxide solution, the bromide and hypobromite are formed:

$$Br_2 + 2KOH \rightarrow KBr + KBrO + H_2O.$$

When the solution is heated, the hypobromite turns into bromate and bromide. The actions are exact parallels of the corresponding ones for chlorine.

Aqueous bromic acid may be made in the same way as chloric acid (p. 274), or by the action of chlorine and water on bromine:

$$5Cl_2 + 6H_2O + Br_2 \rightarrow 2HBrO_3 + 10HCl.$$

The solution is colorless and has powerful oxidizing properties. Thus, it converts iodine into iodic acid.

$$2HBrO_3 + I_2 \rightarrow 2HIO_3 + Br_2.$$

It appears, therefore, that iodine has more affinity for oxygen than has bromine.

Oxides and Oxygen Acids of Iodine. — The following are the acids and their corresponding salts:

[HIO	Hypoiodous acid],	[KIO	Potassium hypoiodite],
HIO_3	Iodic acid,	KIO_3	Potassium iodate,
[HIO_4	Periodic acid],	$NaIO_4$	Sodium periodate,
H_5IO_6	Periodic acid,	$Na_2H_3IO_6$	Disodium periodate.

The substances in parenthesis have not been isolated. There is one oxide, I_2O_5.

Iodates and Iodic Acid. — The potassium and sodium salts of iodic acid are found in Chili saltpeter. They may be made, in much the same fashion as are the chlorates and bromates (p. 272), by adding powdered iodine to a hot solution of potassium or sodium hydroxide. There is evidence that hypoiodites are formed in cold solutions, but they change quickly to iodates.

Iodic Acid is formed by passing chlorine through powdered iodine suspended in water. The action is parallel to that of chlorine on bromine water. A still better way is to boil iodine with aqueous nitric acid (*q.v.*). The latter gives up oxygen readily, and is here used solely on this account. Hence it may be omitted from the equation, only the oxygen, of which it is the source, appearing:

$$I_2 + H_2O + 5O \rightarrow 2HIO_3.$$

In both these actions the initial substances (including the excess of nitric acid) and the products, with the exception of the iodic acid itself, are all volatile. When the solution is concentrated by evaporation, the iodic acid crystallizes. It is a white solid, perfectly stable at ordinary temperatures, and can be kept indefinitely. At 170° it begins to give off water vapor ($2HIO_3 \rightleftarrows H_2O + I_2O_5$), leaving the pentoxide of iodine. The latter is a white crystalline powder which may be raised to 300° before it, in turn, breaks up, giving iodine and oxygen.

In aqueous solution iodic acid is an oxidizing agent, but does not part with its oxygen so readily as do chloric acid and bromic acid. It oxidizes hydrogen iodide in dilute solution:

$$HIO_3 + 5HI \rightarrow 3H_2O + 3I_2,$$

all the iodine being liberated. In this respect it resembles concentrated sulphuric acid (p. 237). Dilute sulphuric acid shows no oxidizing qualities.

Various Acids Derived from One Anhydride.—Some acids are related to their anhydrides as are hypochlorous acid (p. 268) and sulphurous acid (p. 71). One molecule of the anhydride combines with one molecule of water. In other cases, however, the proportion of water may be less or greater than this. Thus phosphoric anhydride (P_2O_5) takes up three formula-weights of water (p. 71). Now if periodic acid were of the former type ($H_2O, I_2O_7 = 2HIO_4$), its formula would be HIO_4. It does form *salts* of this type, such as $NaIO_4$ and $AgIO_4$. But the free acid is a deliquescent solid of the formula H_5IO_6 ($= 5H_2O, I_2O_7$), and the most easily prepared salt belongs to this type. *All types are called periodates, however, because their compositions are all founded upon the same anhydride.* The latter has not itself been made. We usually speak of various acids and salts as being **derived from** the same anhydride, the word "derived" being used in a figurative and not a literal sense.

The difference between two acids HIO_4 and H_5IO_6 is not at all the same as between HIO_3 and HIO_4. The latter would represent different stages of oxidation, being derived from I_2O_5 and I_2O_7 respectively, and accordingly would be named iodic acid and periodic acid. The former differ only by $2H_2O$, and an addition or subtraction of the two elements of water *in equivalent quantities* is neither oxidation nor reduction. Hence they are both periodic acids (see Phosphoric acid).

Periodates and Periodic Acid.—Sodium periodate ($NaIO_4$) is found in Chili saltpeter. When sodium iodate ($NaIO_3$) is dissolved along with sodium hydroxide in water, and chlorine is passed into the mixture, the sodium hypochlorite formed from the latter oxidizes the iodate ($NaIO_3 + O \rightarrow NaIO_4$). But the somewhat insoluble salt which crystallizes out is $Na_2H_3IO_6$:

$$NaIO_3 + O + NaOH + H_2O \rightarrow Na_2H_3IO_6.$$

Other salts may be made from this one.

An aqueous solution of periodic acid is obtained, like that of chloric acid (p. 274), by the action of sulphuric acid on barium periodate. A white, very soluble solid (H_5IO_6) remains when the liquid is evaporated. When this is heated, water and oxygen are both given off, and iodine pentoxide (I_2O_5) alone remains.

Chemical Relations.—The compounds of the halogens with metals and with hydrogen diminish in stability, with ascending atomic weight of the halogen, in the order: F(19), Cl(35.5), Br (80), I (127). Each halogen will displace those following it from this kind of combination. In the case of the oxygen compounds, the order of stability is just the reverse, those of iodine, for example, being the only ones which are reasonably stable. The order of displacement in such compounds confirms this conclusion.

Amongst the oxygen acids of any one halogen, those containing most oxygen are most stable. The salts are in all cases more stable by far than the corresponding acids.

The halogens when combined with metals and hydrogen are univalent (HI, KCl, etc.). It is clear, however, that, when united with oxygen, their valence is higher. The maximum is shown in perchloric anhydride (Cl_2O_7), where chlorine appears to be heptavalent.

The formulæ of the acids might be written so as to retain the univalence:

$$H-Cl, \quad H-O-Cl, \quad H-O-O-Cl, \quad H-O-O-O-Cl,$$
$$H-O-O-O-O-Cl.$$

But compounds in which we are *compelled* to believe that two oxygen units are united are usually unstable (see Hydrogen peroxide), and we should expect the instability would be greater with three and with four units of oxygen in combination. Here, however, the reverse state of affairs must be taken account of in our formulæ, for $HClO_4$ is the

most stable of the chlorine set. This reasoning, together with the heptavalence in Cl_2O_7, leads us to assume the valence seven in perchloric acid (see Periodic system). The structural formulæ (*cf.* p. 224) of some of these substances are therefore often written as follows:

$$\mathrm{H-Cl}, \qquad \mathrm{H-O-Cl}, \qquad \mathrm{H-O-}\overset{\displaystyle \mathrm{O} \atop \displaystyle \|}{\underset{\displaystyle \| \atop \displaystyle \mathrm{O}}{\mathrm{Cl}}}\mathrm{=O}, \qquad \mathrm{Na-O-}\overset{\displaystyle \mathrm{O} \atop \displaystyle \|}{\underset{\displaystyle \| \atop \displaystyle \mathrm{O}}{\mathrm{I}}}\mathrm{=O}.$$

Exercises.—1. Assign to its proper class (p. 187) each of the actions mentioned in this chapter.

2. Knowing that potassium fluosilicate (K_2SiF_6) is insoluble, how should you make chloric acid (p. 265)?

3. Make the equation for the interaction of chlorine with calcium hydroxide in hot water (p. 266). How should you make zinc chlorate from zinc hydroxide ($Zn(OH)_2$)?

4. How should you make pure potassium hypochlorite from hypochlorous acid (p. 268)?

5. On what circumstances would the possibility of making barium chlorate by action of chlorine on barium hydroxide depend (p. 274)?

6. Make the equations for: (*a*) the preparation of potassium bromate; (*b*) pure aqueous bromic acid; (*c*) the interaction of iodine with aqueous potassium hydroxide in the cold, and when heated.

7. Using the method given on p. 274, make the equations for the interactions of chlorine dioxide with water, and with aqueous potassium hydroxide.

CHAPTER XVII

DISSOCIATION IN SOLUTION

THE employment of interacting substances in the form of solutions is so constant in chemistry, and the reasons for this are so cogent, that we must now resume the discussion of the subject of solution (*cf.* p. 145).

The present chapter will be devoted to giving the proofs that, to speak in terms of the molecular hypothesis, the molecules of **acids, bases, and salts** in aqueous solutions, are **actually dissociated into parts** by the solvent. This will be shown by consideration, successively, of certain peculiarities in the **chemical behavior**, the **osmotic pressures**, the **freezing-points**, and the **boiling-points** of the solutions of these substances. We shall see that these parts **coincide in composition with the radicals**, and are called **ions**. Finally, the principles of **chemical equilibrium** will be applied to the relations of the ions to that proportion of the molecules which has remained undissociated.

Some Characteristic Properties of Acids, Bases, and Salts, Shown in Aqueous Solution. — Acids all contain hydrogen (p. 93). In aqueous solution, if soluble, they are sour in taste, they turn blue litmus red, and their hydrogen is displaced by certain metals (p. 95), and has the properties of a radical. By the last statement is meant that it very readily exchanges places with other radicals in reversible double decompositions (p. 264). Many other bodies, like sugar, kerosene, and alcohol, contain hydrogen also, but not one of them shows all of these properties. Again, all salts are made up of two radicals, and the reversible double decompositions into which they enter with acids, bases, and other salts, consist in exchanges of these radicals. Other substances may include the same combination of atoms, but in their actions these groupings are often disregarded. Thus, sodium chloride and silver nitrate exchange radicals completely (p. 13), and, in dilute solution, hydrogen chloride and sodium hydrogen sulphate do so partially (p. 180). But sodium chloride and nitroglycerine $C_3H_5(NO_3)_3$ do not interact at all. The latter is not a salt, although it contains the same proportion of nitrogen to oxygen as does any nitrate.

Furthermore, it is chiefly *in aqueous solution* that these special properties of acids, bases, and salts become apparent. Their behavior is often quite different in the absence of this solvent. If, for example, we mix together ammonium carbonate and anhydrous cupric nitrate, and apply heat, a violent interaction begins. An immense cloud of smoke and gas is thrown out of the tube, and the substance remaining is either black or reddish, in parts, according to the proportions of the substances employed. The residue contains cupric oxide, and sometimes red cuprous oxide (Cu_2O). The gas is tinged red by the presence of nitrogen peroxide (NO_2), while a more careful examination would show that it contained carbon dioxide, nitrogen, nitrous oxide (N_2O), water vapor, and perhaps still other products. The contrast, when the substances are dissolved in water before being brought in contact with one another, is very great. A pale-green precipitate is formed at once, and rapidly settles out. On examination, this turns out to be cupric carbonate, while evaporation of the solution furnishes us with ammonium nitrate. There are only two main products, and the essential part of the action in solution is represented by the equation:

$$(NH_4)_2CO_3 + Cu(NO_3)_2 \rightarrow CuCO_3 + 2NH_4NO_3.$$

In the interaction between the dry substances the molecules are completely disintegrated, and the whole change is very complex. In the action in water no heating is required, the substances are neatly broken apart, certain groups of atoms, which we call radicals, are transferred as wholes from one state of combination to another, and the rearrangement takes place in a machine-like manner. Contrasts like this between the interactions of anhydrous and dissolved bodies are very common. Thus, we have had occasion (p. 96) to mention the difference between the action of metals on concentrated and on dilute sulphuric acid.

Many compounds, however, do not show any change in behavior when dissolved in water. Sugar, for example, is, as a rule, more readily acted upon in the absence of any solvent. Then again, while water is not the only solvent which has the effect we have just described, the majority of solvents, if they affect chemical change at all, simply retard it. Thus the union of iodine and phosphorus in the absence of a solvent takes place spontaneously with a violent evolution of heat. When the elements are dissolved in carbon bisulphide before being mixed the action is much milder, although the product is the same

(phosphorus tri-iodide). The diminution in the concentration of the ingredients has decreased the speed of the action in the normal way (p. 249). That water and some other solvents have a specific influence tending to increase the activity of certain classes of substances, shows that a special explanation of the phenomenon must be found.

Summing up these points we see that the peculiarity of acids, bases, and salts *in aqueous solution* is that each compound always splits in the same way. Thus, cupric nitrate always gives changes involving Cu and NO_3 and never interacts so as to use CuN_2 and O_3, or CuO_2 and NO_2, as the basis of exchange. Similarly, acids always offer hydrogen in exchange, and so nitric acid behaves as if composed of H and NO_3, and sulphuric acid as if composed of 2H and SO_4, and never as if made up of HSO and HO_3, or H_2S and O_4. The sour taste and the effect upon litmus seem to be properties of this easily separable hydrogen, for they are shown only by acids. The result is that we can make a list of the units of exchange, such as H, OH, NO_3, CO_3, SO_4, Cu, K, and Cl, employed by acids, bases, and salts in their interactions. The molecule of each compound of these classes contains at least two of them. Even when these units contain more than one atom, their coherence is as noticeable within this class of actions, as is the permanence of the atomic masses themselves in all actions.

The question raised in our minds is whether solution in water alters the character of the molecule simply by producing a sort of *plane of cleavage* in it which creates a predisposition to a uniform kind of chemical change, or whether it *actually divides* the molecules into separate parts consisting of the above units of exchange, and leaves subsequent chemical actions to occur by cross-combination of these fragments. The fact that the dissolved substances can be recovered by evaporation of the liquid does not demonstrate that they have not been changed temporarily while in solution. The alteration which the water produces, whatever it be, will naturally be reversed when the water is removed. Since our question involves nothing but the counting of particles, the number of which would be much greater in the event that actual subdivision of molecules is the explanation, it can be answered by a study of the physical properties of solutions.

Osmotic Pressure.

In the earlier discussion of solution (p. 150) the condition of a dissolved substance was viewed as akin to that of a gas. We conceived the molecules of the dissolved substance as being distributed

through the space occupied by the solvent, as being separate from one another, and as moving about independently of each other. This was because the phenomena of diffusion and osmotic pressure (p. 151) in solution closely resemble those of diffusion and gaseous pressure in gases.

The invention of a suitable hypothesis for the explanation of the facts of osmosis presents some difficulties, but the facts themselves are undoubted. It will conduce, therefore, to clearness if we speak first of some things which may be observed and are true, irrespective of any explanation.

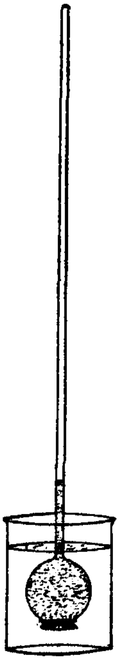


Fig. 73.

Phenomena Produced by Osmotic Pressure. — In order that the osmotic pressure (Gk. ὠσμός, impulsion) of the molecules of a diffusing body may be perceived, a partition, which they are unable to traverse, must be interposed between the solution and a contiguous mass of the pure solvent (Fig. 57, p. 151). The partition must be permeable by the solvent, however. Such a partition is described as **semi-permeable.**

The general nature of the phenomena may be seen by using an inverted thistle-tube (Fig. 73), with the opening covered by a piece of the prepared peritoneal membrane of oxen, and using sugar as the dissolved body. This membrane is not strong enough to serve for measurement. It is also somewhat permeable by the sugar. But the water traverses it very easily, and so an exhibition of the general result of a stricter test is obtained quickly. The bulb of the tube is suspended in pure water.

The water is able to pass freely through the membrane in either direction, while the sugar is not. As the result of the interchange of water, the liquid rises slowly but steadily in the tube. **The pure solvent always passes into the solution.** If, further, two solutions of different concentrations of the same substance are employed, then, invariably, **water passes from the more dilute solution into the more concentrated one** through the membrane. There is apparently a tendency for the water so to distribute itself that the solutions may eventually become equal in strength. The water passes from a dilute solution, leaving it more concentrated than before, into a more concentrated solution, rendering it more dilute.

These phenomena were first studied by Pfeffer (1877), a botanist, who used certain plant cells for the purpose. The cell content included a liquid containing various salts in solution, and a protoplasmic layer which was not attached to the cell wall. This protoplasmic layer behaved like a semi-permeable membrane. When such cells were immersed in a *concentrated* solution of any substance, *the water passed* from the interior of the cell *to the solution*, and by means of a microscope a shrinkage of the protoplasmic layer away from the cell wall could be observed. Conversely, when such cells were placed in pure water, *or a solution of a very dilute nature, water passed* from the outside *into* the interior, and the protoplasmic layer was distended so as to fill the corners completely. The distension of the cells of drooping flowers, when their stems are placed in water, and the consequent revival, is a familiar illustration of the same sort of thing. All solutions which produced neither the one effect nor the other on a given set of plant cells, were named *is-osmotic*. The osmotic pressures of their contents were the same as the pressure of the cell fluid.

Professor Crum Brown has devised an arrangement which exhibits the action of a perfectly semi-permeable membrane very strikingly. A concentrated solution of calcium nitrate is shaken with a small amount of phenol (carbolic acid), so as to become saturated with the latter, and the mixture is then poured into a tall, narrow cylinder. The phenol rises and floats upon the surface of the calcium nitrate. The amount of phenol should not be more than sufficient to saturate the liquid and give a layer a few millimeters in thickness. Distilled water, also saturated with phenol, is cautiously introduced above all. The water on both sides of the layer of phenol is soluble in phenol, and consequently, by dissolving in this and passing out on the other side, can traverse the partition. The calcium nitrate, however, which is here the dissolved substance, cannot traverse the phenol in which it is not soluble. The phenol therefore constitutes a perfect semi-permeable membrane. If the level of the lower side of the phenol is marked on the outside of the cylinder by means of a strip of paper, it will be found, as the arrangement is watched from day to day, that the water passes through the phenol into the solution, and the phenol rises higher and higher, until finally it surmounts all the rest of the liquid.

The Phenomena a Logical Consequence of Semi-Permeability. — The passage of the water *into* the solution in which the greater osmotic pressure exists seems at first paradoxical. We must remember, however, that the system, consisting of the liquids on each side of the membrane, can be in equilibrium only when the osmotic pressure on the two sides is identical. But the equalization of the osmotic pressures cannot take place by the passage of part of the solute from one side to the other. The membrane has been taken,

purposely, of such a nature that the dissolved substance is unable to traverse it. The equalization must occur, therefore, in the only other possible manner, namely, by the passage of the solvent in the other direction.

An imitation of this behavior may easily be exhibited by the use of gases. A piece of peritoneal membrane is stretched across the mouth of a thistle-tube and moistened with water. The tube, which has been bent in U-form to serve as a manometer, contains a small amount of some colored liquid, whose motions will exhibit any change in pressure in the interior. When an inverted cylinder of ammonia gas is placed round the head of the thistle-tube, the ammonia gas dissolves in the water on the membrane until this water is saturated, that is, until the ammonia molecules leaving the water are as numerous as those entering it. It will be seen, however, that the ammonia solution really has two surfaces, one of them towards the interior, and the ammonia particles must eventually leave both surfaces at the same rate at which they are landing upon one of them. The ammonia gas being at the pressure of the atmosphere, the particles of ammonia leaving the film will produce a tension of one atmosphere of ammonia over each surface. Thus ammonia gas will be transferred from the cylinder to the interior of the thistle-tube until its partial pressure in the latter is equal to that in the former. The membrane is semi-permeable, since, of the air and ammonia contained in the thistle-tube, only the ammonia can traverse the film. The contents of the thistle-tube therefore correspond to the solution, air being the solute and ammonia the solvent. The original air in the apparatus was at a pressure of one atmosphere, but the ammonia, although under no greater pressure, enters nevertheless. Indeed, it would continue to do so until the pressure inside became equal to that of the ammonia outside plus the original pressure of the air, a total of two atmospheres. The case corresponds to that of water entering a solution whose osmotic pressure is one atmosphere. It enters until the contents of the apparatus are under a pressure one atmosphere greater than that existing outside.

Measurement of Osmotic Pressure. — It will be seen that the whole phenomenon rests upon the fact that the membrane used is permeable by one of the constituents only. The preparation of a vessel of sufficient strength, and possessing walls with the maximum permeability by water and the minimum permeability by dissolved substances, presents great difficulties. A device of Pfeffer's is still found to be the best. A cylinder of porous porcelain, much like a Pasteur filter-tube, is treated so that its pores are partially filled with a gelatinous precipitate of cupric ferrocyanide (*q.v.*).

The porous cylinder, after removal under the air-pump of the air which its walls contain, is placed in a solution of cupric sulphate. Its interior is then filled with a solution of potassium ferrocyanide. When these two liquids meet by diffusion inside the wall, they interact, producing a dense precipitate of the substance above mentioned:

$$2CuSO_4 + K_4Fe(CN)_6 \rightarrow Cu_2Fe(CN)_6 + 2K_2SO_4.$$

If such a prepared vessel, after being filled with a one per cent sugar solution, could be closed by a piston (*e.g.* Fig. 46) and be placed in pure water, it would be found necessary to place weights on the piston to prevent an upward movement, due to access of water to the interior through the walls. Finally a weight would be found that would just balance the inward tendency of the water. With more weight than this, water would be squeezed out through the pores; with less, the water would force its way in and the piston would rise. When this weight has been placed in position, the *water* inside and outside, having reached a condition of equilibrium, must be exerting equal pressures on each side of the wall of the vessel. Hence, the excess of pressure inside must be due to the osmotic pressure of the dissolved sugar. It cannot be due to the water itself, for that is able to escape through the pores. The weight opposing the osmotic pressure at 15° in the case of a one per cent sugar solution is found to be about 0.7 kg. for every sq. cm. of the exposed surface. Since 1.03 kg. per sq. cm. equals 760 mm., this would indicate a pressure of $760 \times 0.7 \div 1.03$, or 516 mm. (0.68 atmospheres).

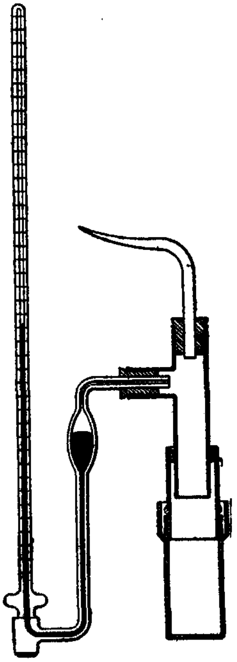


FIG. 74.

In practice a small bent tube opening into the cylinder is used as a manometer (Fig. 74). The other end of the tube is closed, and some air is confined in this end by mercury. The diminution in the volume of the air registers the pressure. The smaller tube, drawn out to a point, is used for filling the cell with the solution and is then sealed before the blowpipe. The whole apparatus is immersed in a large bath of water whose temperature can be maintained constant during the experiment. Concordant readings are hard to get in consequence of difficulties inherent in the preparation and use of the apparatus, but the general relations of the results can be stated in a very simple form.

Ten years after Pfeffer's experimental work, van 't Hoff first formulated the laws of osmotic pressure. He showed that the general analogy between the gaseous state and the state of solution could be developed so as to exhibit a complete

correspondence between the laws of both. His conclusions (1887) were founded partly on Pfeffer's results and partly on supplementary experiments, and are given in the three following paragraphs (see, also, appendix to this chapter).

Osmotic Pressure and Concentration. — A part of one of Pfeffer's sets of experiments will show the relation in this respect:

Per Cent of Sugar.	Osmotic Pressure.	Per Cent of Sugar.	Osmotic Pressure.
1	535 mm.	4	2082 mm.
2	1016	6	3075

The osmotic pressures of a series of solutions of the same substance are proportional to their concentrations. The form of the law is the same as that of Boyle's law (p. 81). The pressures are in general the same for the same concentrations whatever solvent is used.

Osmotic Pressure and Temperature.—Pfeffer, using a one per cent solution of sugar at two different temperatures, found the pressure at 14.2° to be 510 mm. and at 32° to be 544 mm. Not only does osmotic pressure change, with alteration in temperature, in the same direction as does gaseous pressure, but the changes can be expressed by Charles' law (p. 87). **The osmotic pressure increases in proportion to the absolute temperature.** A *gas* which at 14.2° C. exhibits a pressure of 510 mm., at 32° exercises a pressure of 542 mm.

An Analogue of Avogadro's Hypothesis. —Still more interesting is the fact that, if we compare the concentrations of different **solutions which at the same temperature exhibit equal osmotic pressures, we find that they contain equal numbers of molecules of the dissolved substance in equal volumes.** Thus, if we dissolve one mole (342 g.) of sugar ($C_{12}H_{22}O_{11}$) and one mole (74 g.) of methyl acetate ($CH_3C_2H_3O_2$) in equal volumes of water, we have taken equal numbers of molecules of the two substances, and the osmotic pressures which the solutions exhibit are found to be equal.

As will be seen below, certain substances in certain solvents, particularly in water, exhibit pressures which are greater than this hypothesis would permit.

The closer study of the figures enabled van 't Hoff (1887) to state the most interesting fact of all: **The osmotic pressure exercised by a substance in solution is identical in value with the gaseous pressure**

which it would exhibit if the same quantity of it were contained as a gas in the same volume at the same temperature. For example, 44 g. of carbon dioxide in the gaseous condition fills the G.M.V. (22.4 l.), and at 0° exercises a pressure of one atmosphere. We find that when we dissolve the same quantity of the same substance in 22.4 l. of any solvent at the same temperature, it exercises one atmosphere of osmotic pressure. Certain substances, however, particularly when dissolved in water, exhibit greater pressures than this (see below).

Determination of Molecular Weights. — It is evident that we have here an experimental method which may be used in measuring the molecular weight, and is applicable to substances which cannot be converted into vapor. All that is necessary is to dissolve a weighed amount of the substance in a known amount of water, or some suitable solvent, and by means of the apparatus described above to measure the osmotic pressure at some fixed temperature. From the result, by means of the laws corresponding to those of Boyle and Charles, we may calculate the concentration of the solution which would have given one atmosphere pressure at 0°. That quantity of substance which would give this concentration in 22.4 l. of the solvent is then the molecular weight (*cf.* p. 199). The time required for measurements of osmotic pressure and the experimental difficulties alone prevent the employment of this method in practice.

Osmotic Pressure and Dissociation in Solutions. — What inference is to be drawn in the cases in which abnormally high osmotic pressures are observed? In view of the fact that the pressure is supposed to be produced by the impact of the particles, and depends on the number of them in the given volume, we must infer that where the pressure is greater, more particles are present in the given volume than we had supposed. In other words, dissociation of the original molecules must have occurred. This phenomenon is observed whenever acids, bases, or salts in aqueous solution are under observation. Thus a solution of sugar, which does not belong to these classes, containing 342 g. in the G.M.V., exhibits the normal osmotic pressure of one atmosphere at 0°. A solution of one molecular weight of potassium chloride (74.5 g.) in the same volume of water, however, exhibits an osmotic pressure of about 1.88 atmospheres at 0°. The greater pressure must be due to the fact that, although the number of *molecules* of potassium chloride taken is the same as in the case of sugar, the number of *actual particles* whose impacts constitute the pressure is greater, — is, in fact, 88 per cent greater. Now the multiplication of particles from potassium chloride molecules can occur only by their

dissociation into particles of K and Cl by a chemical change represented by the equation $KCl \rightleftarrows K + Cl$. In this case, seeing that each original molecule can give but two particles, the excess of pressure indicates that 0.88 (88 per cent) of the molecules of potassium chloride have been broken up. Comparison shows that the degree of dissociation for equi-molar solutions of different acids, bases, or salts varies widely. For the same substance, it is always relatively greater in dilute than in concentrated solutions.

It will be seen that we have thus a purely physical and perfectly independent confirmation of the indications already found in the chemical behavior of substances of this kind. In practice, on account of the experimental difficulties, this method is not used for measuring the degree of dissociation.

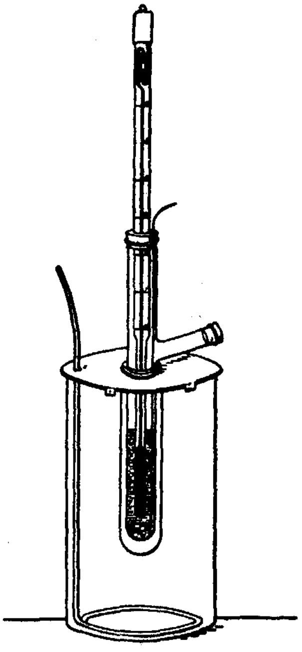


FIG. 75.

DEPRESSION IN THE FREEZING-POINT OF A SOLVENT.

Measurement of Freezing-Points. — The task consists in measuring exactly the temperature at which a previously weighed quantity of the solvent freezes, and then, after dissolving in it a known weight of some soluble substance, determining the freezing-point once more. The absolute values of these two points are not required, it is simply the difference between them that has to be known with exactness (*cf.* p. 163). By means of a very delicate thermometer (Fig. 75) having only six degrees on the whole scale, the temperature of the freezing liquid may be read to one one-thousandth of a degree. A reservoir at the top enables us to add to, or subtract from, the mercury contained in the bulb and column, and so the same instrument may be used with solvents having widely different freezing-points. When water is being employed as the solvent, the outer jar must be filled with a freezing mixture of ice and water containing salt. With solutions in benzene, ice and water are used alone. To avoid super-

cooling, the solvent or solution must be vigorously stirred **after** it has been cooled down to a point just below the freezing-point.

Laws of Freezing-Point Depression. — The depression is directly proportional to the weight of dissolved substance in a given amount of the solvent. The depression is inversely proportional to the amount of solvent. Thus, if we double the concentration of the solution, the depression in the freezing-point is doubled. Further, equal numbers of molecules of different solutes in the same quantity of solvent give equal depressions. Or, in other words, the depression is proportional to the concentration of the molecules of the solute. Thus, solutions containing 342 g. of sugar ($C_{12}H_{22}O_{11}$), or 46 g. of alcohol (C_2H_6O), or 74 g. of methyl acetate ($CH_3C_2H_3O_2$), in 1000 g. of water, show a depression below the freezing-point of water of 1.89° in each case. This depression produced by a mole of the solute in 1 l. of water is called the **molecular depression constant** and has a different value for each solvent. For solutions of the same molecular concentration in benzene the depression is 4.9°, in phenol (carbolic acid) 7.5°. Combining these facts in one expression:

$$\left.\begin{array}{r}\text{The observed depression}\\ \text{in an aqueous solution}\end{array}\right\} = 1.89^\circ \times \frac{\text{Wt. of Solute}}{\text{Mol. Wt. of Solute}} \times \frac{1000}{\text{Wt. of Solvent.}}$$

For other solvents, the corresponding value of the depression constant must be substituted for 1.89°.

These principles may be expressed mathematically in a form which is convenient for use. If Δ represent the depression in any actual experiment, δ the depression produced by one molecular weight in 1000 grams of solvent, W the weight of the substance, M its molecular weight, and g the weight of the solvent in grams, then:

$$\Delta = \delta \times \frac{W \times 1000}{M \times g}.$$

In the case of water, as we have seen, δ is 1.89°. For each solvent the value of δ must be determined by means of a substance of known molecular weight.

These laws describe the facts most exactly when the solutions are dilute. They hold only when there is no chemical interaction between solute and solvent. Even so, however, acids, bases, and salts dissolved in water present many apparent exceptions and must be discussed separately.

Determination of Molecular Weights. — When the depression constant of a solvent has once been ascertained by means of a substance of known molecular weight, this method may be used for determining the molecular weight of other substances which are soluble in the same liquid. All the other factors can be observed and substituted in the formula. This method is especially useful when the substance cannot be converted into vapor without undergoing decomposition (see Hydrogen peroxide).

Freezing-Points and Dissociation in Solution. — The substances which present the most conspicuous exceptions to the above rules are acids, bases, and salts in aqueous solution. With most of these, the depression produced is greater than we should expect from the concentration of the solution. Thus, in an actual experiment, two equi-molar solutions were compared. One contained one mole (74 g.) of methyl acetate, and the other one mole (58.5 g.) of sodium chloride, each dissolved in 2000 g. (2 liters) of water. The freezing-points observed, on the arbitrary scale of the thermometer, were:

Pure water	3.580°	Pure water	3.580°
Solution of methyl acetate	2.610°	Solution of salt	1.902°
Depression	0.970°	Depression	1.678°
			0.970°
		Excess depression by salt	0.708°

The solution of methyl acetate, as it contained only 0.5 moles of the solute per liter of water, showed, as it should do, about half the average molecular depression (1.89°, p. 291). This is typical of the class of substances showing normal behavior. Sugar, alcohol, and hundreds of other substances, in solutions of the same molar concentration, would have given the same value.

The freezing-point of the salt solution, however, was much lower. If this solution had contained the same concentration of dissolved particles as the other solution, its depression would have been 0.970° likewise. The number of particles must therefore have been greater than we should have expected from the number of molecules taken. In other words, a portion of the molecules of the salt must have been broken up, and the excess depression, 0.708°, must have been due to the extra particles produced by dissociation. Now sodium chloride molecules cannot give more than two particles each, and the depression is proportional to the number of particles. It follows, therefore, that $\frac{708}{970}$, or 0.732 (73.2 per cent) of the molecules were dissociated.

This result is typical also. Acids, bases, and salts of which one mole is dissolved in two liters of water, are found to give irregular values, all more or less in excess of 0.970°. Those which contain but two radicals, like sodium chloride ($NaCl$) and potassium nitrate (KNO_3), give values between 0.970° and 2 × 0.970°. Substances like calcium chloride ($CaCl_2$) and sodium sulphate (Na_2SO_4) give depressions approaching three times the normal value: their molecules contain three radicals. The excess depression depends, therefore, upon the number of particles which each molecule can furnish, and upon the proportion of all the molecules which is dissociated into these fragments.

In the case of an acid, base, or salt, the depression is not strictly proportional to the concentration. Thus, one mole of salt in four liters of water does not give half the depression of the two-liter solution (0.839°) but somewhat more (about 0.844°). The same method of calculation indicates, therefore, a greater degree of dissociation (about 79 per cent) in the more dilute solution (see Ionic equilibrium, below).

Acids, bases, and salts, so far as they are soluble in materials like toluene, benzene, chloroform, and carbon bisulphide, exhibit simply normal depressions in these solvents. It appears, therefore, that dissociation does not take place in many solvents. In common experience it is encountered only in solutions in water, and, perhaps, alcohol.

Boiling-Points and Dissociation in Solution. — If space permitted, a series of statements might be made in regard to the boiling-points of solutions (*cf.* p. 162) which would be closely parallel to those about freezing-points. The boiling-point, as we have seen, is **elevated**, however, by the introduction of a foreign body. Thus, when water is the solvent, one mole of a solute in 1000 g. of the solvent normally raises the boiling-point 0.52° (that is, from 100° to 100.52°). But acids, bases, and salts form an exception to this rule, as before, and the excess elevation which they give is a measure of the degree of dissociation.

Comparison of the Results of the Three Methods. — When we measure the osmotic pressure, the freezing-point depression, and the elevation in the boiling-point of the same solution, and calculate the degree of dissociation from the result of each measurement, we find

that the values obtained are usually identical, within the limits of error to which the methods are liable. Indeed, the theory of this subject, developed by van 't Hoff, enables us to connect the osmotic pressure by a mathematical relation with the other two phenomena, and to calculate any one of the three from any other.

The connection between the three sets of phenomena cannot be explained here. It is treated in all works on Physical Chemistry. It may be pointed out, however, that, in one essential respect, experiments in osmotic pressure, and in the freezing and boiling of solutions, are all alike. The perception of osmotic pressure involves a partition which the solvent alone can pass, and the osmotic pressure for a given solution is the one required to force the solvent out. In freezing a solution, *pure ice* is separated, and so a similar extrusion of a part of the pure solvent is effected. In a boiling solution, for which the above rules hold, the vapor is composed of the pure solvent, and the solute remains behind. *The relation between the three operations lies in the fact that in each case the same thing,* namely, the separation of a part of the solvent, is done. Each method effects this in a different way. But the expressions representing the work done, in terms of the factors which define the work in each case, can be equated in pairs and the required relation established. Thus the molecular depression of the freezing-point, or the molecular elevation in the boiling-point, as we have defined them, is equal to $0.002\ T^2 \div q$, where T is the absolute temperature of the freezing- or boiling-point, and q is the heat of fusion or vaporization, as the case may be. Water, for example, freezes at 273° abs., and its heat of fusion is 79 cal. per gram, from which the calculated molecular depression, $0.002 \times 273^2 \div 79$, or 1.88°, is obtained. Similarly, using the boiling-point, 373° abs., and the heat of vaporization, 537 cal. per gram, we calculate the molecular elevation of the boiling-point to be 0.518°.

It ought to be added that *abnormally small* osmotic pressures, freezing-point depressions, and boiling-point elevations, are also frequently observed. This occurs, however, almost wholly in non-aqueous solvents, such as benzene. It is shown particularly by substances containing oxygen, and is even noticed in the case of acids, bases, and salts. By parity of reasoning we infer that in these cases ***association*** (*cf.* p. 242) of the molecules has occurred, and that the physical unit of the solute in these solvents is larger than the ordinary molecule.

The Application of these Conclusions in Chemistry.

The Constitution of Solutions of Acids, Bases, and Salts.—The composition of solutions which are normal or abnormal, in respect to osmotic pressure, freezing-point, and boiling-point, may be shown thus:

Solutes.	Dissolved in Water, Alcohol, etc.	Dissolved in Toluene, Chloroform, etc.
Acids, bases, salts	Abnormal	Normal
Other substances	Normal	Normal

It appears that water and some other solvents have the power of breaking up the molecules of acids, bases, and salts and of holding the fragments apart from one another and hindering their reunion. In consequence of this, our view of the nature of an aqueous solution of hydrogen chloride (HCl), or common salt (NaCl), or sodium hydroxide (NaOH), or any of the substances of the classes which these represent, may now be stated in definite terms. Such a solution contains, besides undivided molecules of the solute, at least two other kinds of material, H, Na,* Cl, OH, etc., which result from the breaking up of the molecules. We shall see that these subdivisions of the original molecules have distinct physical and chemical properties of their own. The descriptions of the "properties" of the solutions, as they used to be given in chemistry, were really a confused statement of the properties of the different constituents of a mixture of molecules and their fragments. Thus the indications of dissociation found in the chemical behavior of acids, bases, and salts (p. 282) are fully confirmed by a study of the physical properties of their solutions.†

The suggestion that the multiplication of particles takes place by interaction of the salt with part of the water, $NaCl + H_2O \rightleftarrows NaOH + HCl$, resulting in the production of two molecules of dissolved matter from one, is open to several fatal objections. In the case of a highly dissociated salt, according to this explanation, the mixing of the acid and base in dilute solution should result in no particular change and give rise, therefore, to no development of heat. But the heat of neutralization is very great in such cases. This is an example of a stochastic hypothesis (p. 142), be it noted, and its verity or falsity can be put to the test at once. Its inapplicability is further seen in the fact that it cannot explain the dissociation of acids and bases themselves.

The *free* radicals, of whose existence we have thus become convinced, constitute a new set of materials. Thus the hydrogen radical of acids, although a form of uncombined hydrogen, differs totally from the gas which is composed of the same material. The latter has no sour taste or effect upon litmus. It is very slightly soluble in water, while the hydrogen radical exists as a separate substance only in solution. Again, substances with the composition of the radicals NO_3 and SO_4 are not known at all except in solutions. The chief peculiarity of these substances is that a solution cannot be made which contains less than two

* The objection that separate atoms of sodium could not remain free in water, will be disposed of later.

† Recent observations, showing that in some cases rapid double decompositions of the normal kind take place in solutions which exhibit no physical evidence of the existence of dissociation, demonstrates that it would have been unsafe to infer dissociation from chemical evidence alone.

kinds of them side by side. A niche, therefore, must be created in our molecular hypothesis to receive these new substances.

Nomenclature: The Ionic Hypothesis. — Our chemical molecules are the units of material in the gaseous condition (p. 198). Evidently smaller units, which may nevertheless contain more than one atom, must be assumed to exist in solution. These units, for a reason that will appear later, are called **ions**, and their composition corresponds to that of the radicals. The dissociation of molecules into ions is named **ionization**. The substances of the three classes which alone are ionized may be designated **ionogens**. Since ions are discrete particles, they are, in all physical respects, molecules. Thus we speak of the *molecular* concentration of ionic hydrogen, just as we do of that of dissolved or of gaseous hydrogen.

The solution of an ionized substance is called an electrolyte (*q.v.*), and often this term is applied also to acids, bases, and salts themselves, because, when dissolved, they produce electrolytes. This is rather a confusing metonymy, however, because these bodies by themselves are *not conductors*. This use of the term also introduces obscurity because it connects the ionization with electrolysis and always conveys the impression that the latter produces the former. The electrolytic property of ions is only one amongst many special properties of electrolytes, and the majority of these properties are chemical and have nothing to do with electrolysis. Hence we have preferred the more general word "ionogen."

The radicals and their chemical behavior are real, and all the peculiarities of aqueous solutions of acids, bases, and salts are experimental facts. Ions, however, like corpuscles, atoms, and molecules, are part of our great system of formulative hypotheses and are added to it in order to maintain its self-consistency. We apply that part of the hypothetical system known as Avogadro's hypothesis to solutions, and finding portions of molecules which do not exist in the gaseous condition and which have special properties of their own, a new class of unit masses has to be established. Molecules are units which are not commonly disintegrated by vaporization (p. 198); ions, those which are not commonly disintegrated in double decomposition in solution; atoms, those which are not commonly disintegrated in any chemical action. But there are exceptions in each of the three cases. The ionic hypothesis was first suggested by Arrhenius (1887) immediately after the publication of van 't Hoff's correlation of the facts about osmotic pressure (p. 288).

It is worth noting that the quantities expressed by the formulæ Al, Ca, and K, when existing as ions, produce equal osmotic pressures, and have equal effects

upon the freezing- and boiling-points. This is a further justification for our choice of chemical unit quantities of the elements (atomic weights), for the atomic weights have these properties in common, and equivalents, of course, do not (*cf.* p. 210).

Ionic Equilibrium. — Since the ions are chemically different from their parent molecules, their formation represents a variety of chemical change. The change does not involve any chemical interaction with the water, of the nature of hydrolysis, for cases in which this takes place are expressly excluded from consideration. It is simply a dissociation, *i.e.* reversible decomposition of the dissolved substance.

From the fact that the proportion of molecules ionized is shown to become greater as more and more of the solvent is added, and that removal of the solvent diminishes the proportion of ions to molecules, and finally leaves us the substance entirely restored to the molecular condition, we know that this is a reversible action and therefore a true dissociation. The molecules and their ions adjust themselves like the constituents in any case of chemical equilibrium. In the cases above mentioned we should have the following actions taking place: *

$$HCl \rightleftarrows H^{\cdot} + Cl' \qquad NaCl \rightleftarrows Na^{\cdot} + Cl' \qquad NaOH \rightleftarrows Na^{\cdot} + OH'.$$

These equilibria are all of precisely the same nature as that of phosphorus pentachloride vapor (p. 255), and the discussion of the latter should be reëxamined and applied by the reader. The sole difference is that here change in volume is effected, not by compression or by release of pressure, but by removing or adding water. The adjustment to a condition of equilibrium, however, seems to be instantaneous where ions are concerned, while in other chemical actions it always takes a perceptible, and often a considerable interval of time.

Using C_1, C_2, and C_3 for the molecular concentrations (numbers of moles per liter) of the molecules, and the two ions, respectively, we have an equilibrium constant (*cf.* p. 254), in this case called the **ionization constant**:

$$K = \frac{C_2 \times C_3}{C_1}.$$

When we dissolve a single substance which gives only two ions, the molecular concentrations of the ions are necessarily equal. Hence, in such a case, $\frac{C_2^2}{C_1} = K$. When some other ionogen with a common ion is present, however, the values of C_2 and C_3 will be different.

* The symbols $Na^{\cdot}$, Cl', etc., are used to indicate that these are ions, and not identical with atoms, Na, Cl, etc. The negative radicals and hydroxyl are distinguished thus, NO_3', OH', and the others by a dot, $H^{\cdot}$, $K^{\cdot}$.

Considering the form of the above mathematical expression, it will be seen that when the degree of ionization is great, C_2 and C_3 are larger than C_1, and the value of K, the ionization constant, will be great. On the other hand, in the case of feebly dissociated substances, the value of K will be small. Furthermore, if by the addition of more water we diminish all the concentrations, this will momentarily affect the numerator more than the denominator (*cf.* p. 298). In order, therefore, that the value of the whole expression may remain constant, the concentrations of the ions, represented by C_2 and C_3, must become greater, and can only do so at the expense of the concentration of the undissociated molecules, represented by C_1. Our formula, therefore, represents successfully the fact that dilution, which diminishes the concentration of all the substances, produces a greater degree of ionization.

A more general form of treatment will be required later. If a be the number of moles, say of acetic acid, originally taken, v the volume of the solution in liters, and x the number of moles ionized, then the molar concentrations at equilibrium will be

$$C_1 = \frac{a - x}{v} \text{ and } C_2 = C_3 = \frac{x}{v}.$$

Therefore,

$$\left(\frac{x}{v}\right)^2 \div \frac{a - x}{v} = K, \text{ or, } \frac{x^2}{(a - x)v} = K.$$

This is known as Ostwald's **dilution formula**.

Exercises. — 1. A one per cent sugar solution gives an osmotic pressure of 516 mm. at 15°. What is the molecular weight of sugar? Assume that the sp. gr. of the solution is 1.

2. What gaseous pressure would be exerted by a gas of the same molecular concentration as a one per cent solution of sugar at 15° (p. 288)? Compare the answer with the osmotic pressure of the solution.

3. What depression in the f.-p. of water will be produced by dissolving 10 g. of bromine in 1 kg. of this solvent?

4. What depressions in the f.-p. of benzene and of phenol would be produced by 10 g. of bromine to 1 kg. of the solvent, if no chemical action took place?

5. What is the molecular depression-constant of a solvent in which 5 g. of iodine in 500 g. of the solvent lowers the f.-p. 0.7°?

6. What is the degree of dissociation of zinc sulphate if 5 g. of it

dissolved in 125 g. of water produce a lowering of 0.603° in the f.-p.? What is the molecular concentration of each of the three substances present in this solution?

7. What will be the approximate b.-p. of a solution of common salt, saturated at 100° (p. 157)? Assume that the solute is 80 per cent dissociated.

Appendix: Recent Measurements of Osmotic Pressure.— Measurements of osmotic pressure by Morse and Frazer, published since the foregoing was written, are the only ones yet made which deal with pressures of more than three or four atmospheres.

The actual measurement is made according to the general method described on p. 287, that is, by means of a porous porcelain cup or cylinder which contains the semi-permeable membrane within its walls, and is attached to a manometer containing an inclosed volume of air over mercury.

The membrane, however, is deposited electrolytically, instead of by diffusion. The method of procedure is briefly as follows: The porous cylinder, after the removal of the air from its walls by "electrical endosmose," is surrounded by a copper electrode, and both cup and electrode are immersed in a 0.1 N solution of copper sulphate. The other electrode, the anode, is placed within the cup, which is filled with a 0.1 N solution of potassium ferrocyanide. A current of electricity with an electromotive force of 110 volts is then passed through the solutions and the porous wall of the cylinder, from the copper to the platinum electrode, and the membrane of copper ferrocyanide is deposited either upon the interior surface of the cup, or within its walls. By proceeding in this way, only from one to three hours, instead of several days, are required for the formation of a suitable membrane.

The following table contains the results of some measurements made with solutions of cane-sugar in water. The proportionality between concentration and osmotic pressure is evident.

Moles Sugar in 1000 Grams Water.	Osmotic Pressure (Atmospheres).	Moles Sugar in 1000 Grams Water.	Osmotic Pressure (Atmospheres).
0.2	4.83	0.5	12.15
0.4	9.72	1.0	24.46

From data already obtained by Morse and Frazer, it seems very probable that the statement of one of van 't Hoff's laws (p. 288) will have to be modified, for it is found that "cane-sugar, dissolved in water, exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state" (*Amer. Chem. Jour.*, July, 1905).

CHAPTER XVIII

OZONE AND HYDROGEN PEROXIDE

A FRESH, penetrating odor, resembling that of very dilute chlorine, was noticed by van Marum (1785) as being perceptible near an electrical machine in operation. Schönbein (1840) showed that the odor was that of a distinct substance, which he named ozone (Gk. ὄζειν, to smell), and he discovered a number of ways of obtaining it. It is very questionable whether there is any ozone in the air, excepting temporarily in the immediate neighborhood of a natural or artificial discharge of electricity.

Preparation of Ozone. — The most satisfactory way of preparing ozone (O_3) is to allow electric waves to pass through oxygen. The apparatus (Fig. 76) consists of two co-axial glass tubes, between which the oxygen flows. The waves are generated by connecting an

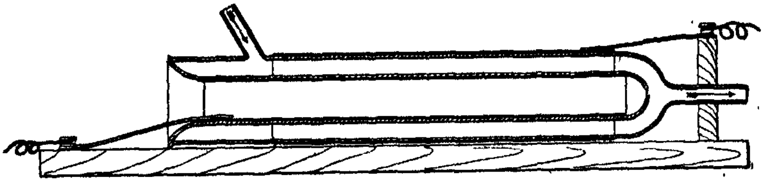


FIG. 76.

outer layer of tinfoil on the outer tube, and an inner layer of tinfoil in the inner tube with the poles of an induction coil. With dry, cold oxygen, about 7.5 per cent of the gas is easily turned into ozone. Under the best conditions this proportion cannot be much exceeded.

Ozone is found in the oxygen generated by electrolysis of dilute sulphuric acid (p. 95). Some of it is produced when sulphuric acid acts upon oxides which, with this reagent, liberate oxygen, *e.g.*, $2BaO_2 + 2H_2SO_4 \rightarrow 2BaSO_4 + 2H_2O + O_2$. It arises during the slow oxidation of phosphorus by the air, resulting, probably, from the decomposition of unstable, highly oxidized bodies which are formed during the action. Oxygen containing as much as 15 per cent of it is produced by the interaction of fluorine and water (p. 241).

Physical Properties of Ozone. — Ozone is a gas of blue color. It boils at $-119°$, so that when a mixture of oxygen and ozone is led through a U-tube immersed in liquid oxygen ($-182.5°$), the ozone is liquefied. The opaque, deep-blue fluid contains only about 14 per cent of oxygen, and this may be removed by evaporation.

Ozone is much more soluble in water than is oxygen. Its solubility shows that, at 12°, 100 volumes of water would dissolve 50 volumes of the gas at one atmosphere pressure. Its solubility, when mixed with oxygen, is in proportion to its partial pressure (p. 155).

Chemical Properties of Ozone. — Ozone is relatively stable only when mixed with much oxygen. Hence its density and molar weight cannot be ascertained save by indirect means. The weight of a liter of the mixture at 0° and 760 mm. having been measured, the ozone may be removed by absorption in turpentine and the proportion of it present in the gaseous mixture be thus ascertained. For example, if the weight of 1 l. was 1.468 g. and 50 c.c. were absorbed by turpentine, there were 950 c.c. of oxygen. The weight of this oxygen is 1000 : 950 :: 1.429 : x, from which $x = 1.361$ g. The rest of the weight, 1.468 − 1.361 or 0.107 g., was that of 50 c.c. of ozone. The weight of 1 l. of ozone at 0° and 760 mm. is therefore 2.140 g. The molecular weight (weight of 22.4 l.) is thus 47.9 g., or nearly 48 g. The formula of ozone is therefore O_3.

When ozonized oxygen is heated, the ozone is decomposed at about 250–300°. The action for its formation:

$$3O_2 \rightleftarrows 2O_3$$

is therefore reversible. That this equation, showing that three molecules of oxygen give two molecules of ozone, is correct, may be demonstrated by measuring the diminution in volume which accompanies the action. If a shrinkage of 5 c.c. is observed in forming the ozone, it is found that 10 c.c. more are then absorbed by turpentine. Thus the ozone occupied 10 c.c., and the total oxygen from which it was made was therefore 15 c.c. Hence three volumes of oxygen give two of ozone.

The formation of ozone absorbs much energy from the electric waves, or, in other methods of making it, from the concomitant chemical changes:

$$O + O_2 = O_3 - 32{,}400 \text{ cal.}$$

Ozone is a much more active oxidizing agent than oxygen. Mercury and silver, which are not affected by the latter, are converted into

oxides by the former. Silver gives the peroxide, Ag_2O_2. Paper dipped in starch emulsion containing a little potassium iodide is used as a test for ozone :

$$O_3 + 2KI + H_2O \rightarrow O_2 + 2KOH + I_2.$$

The iodine gives a deep-blue color to the starch (*cf.* p. 235). This test, however, will not distinguish ozone from chlorine or hydrogen peroxide, and may, therefore, be used only in the absence of these substances. The last substance is always present in the air, and, since air usually shows the above action, is probably responsible for the belief that air contains ozone. The action on silver has never been obtained with air. Ozone also removes the color from organic dyes, such as indigo, by oxidizing them (*cf.* p. 269). Its activity as an oxidizing agent, like the similar activity of hypochlorous acid, is due to the fact that it contains much more energy than oxygen. In all its actions the energy set free is greater by this excess than that liberated when oxygen is used.

Oxygen and ozone are different substances (p. 35), that is, have different properties. The difference in density, interpreted in terms of the molecular hypothesis, gives us the statement of the nature of the difference which is embodied in the formulæ O_2 and O_3. The difference in activity, interpreted in terms of the conception of energy, gives us the other method of stating the nature of the difference. The recent preference for the second method is well illustrated by this case. The first method uses a mere physical property, the second a fact which is intimately connected with the whole *chemical behavior* of the substance, a matter of much greater interest to the chemist.

Ozone may be distinguished from chlorine, nitrogen peroxide, and other oxidizing agents, with the exception of hydrogen peroxide, by using pink litmus paper instead of plain paper to carry the potassium iodide solution in the above test. The potassium hydroxide set free by ozone turns the paper blue. Chlorine, for example, gives an entirely different action : $Cl_2 + 2KI \rightarrow 2KCl + I_2$.

Ozone is used commercially in bleaching oils and in purifying starch. It is employed also for sterilizing drinking water in Lille and other cities.

Hydrogen Peroxide.

Hydrogen peroxide (H_2O_2) is found in minute amounts in rain and snow. It is formed in small quantities, in a way not at present understood, when moist metals rust.

Preparation of Hydrogen Peroxide. — When sodium peroxide (*q.v.*) is added, a little at a time, to a dilute acid, hydrogen peroxide is set free:

$$Na_2O_2 + 2HCl \leftrightarrows 2NaCl + H_2O_2.$$

It may be separated from the salt (and a large part of the water) by repeatedly shaking the mixture with ether (*cf.* p. 155). The relative solubility in water and ether is 1 : 0.0596, however, so that much ether is needed. The ethereal layer, which rises to the top, when evaporated, leaves a strong aqueous solution of the compound behind.

When hydrated barium peroxide (BaO_2, $8H_2O$) is shaken with cold, dilute sulphuric acid a similar action takes place:

$$BaO_2 + H_2SO_4 \leftrightarrows BaSO_4 \downarrow + H_2O_2.$$

The excess of sulphuric acid may be removed by adding barium hydroxide solution cautiously until no further precipitation of barium sulphate occurs: $Ba(OH)_2 + H_2SO_4 \leftrightarrows BaSO_4 \downarrow + 2H_2O$. Hydrochloric acid or phosphoric acid may be used instead of sulphuric acid. The second is largely employed in the commercial manufacture of hydrogen peroxide. In each case, great care has to be taken to precipitate the other products and all impurities from the solution. When hydrochloric acid is used, for example, the barium chloride produced by the action is removed by adding silver sulphate:

$$BaCl_2 + Ag_2SO_4 \leftrightarrows BaSO_4 \downarrow + 2AgCl \downarrow.$$

An aqueous solution is also obtained by passing carbon dioxide through barium peroxide suspended in water:

$$BaO_2 + CO_2 + H_2O \leftrightarrows BaCO_3 \downarrow + H_2O_2.$$

Pure hydrogen peroxide is isolated from any of these solutions by distillation under reduced pressure (p. 276). It is much less volatile than water, but decomposes into water and oxygen violently at 100°. Hence the lower pressure is required to make possible its volatilization at a temperature below this point. At 68 mm. pressure, the water begins to pass off first (at about 45°). The last portion of the liquid boils at 84–85° and is almost all hydrogen peroxide.

By evaporating the commercial (3 per cent) solution at 70°, a liquid containing 45 per cent of hydrogen peroxide may be made without much loss of the material by volatilization.

The Interaction of Barium Peroxide and Sulphuric Acid. — It is worth noting that, although common barium peroxide is not less soluble in water than is the hydrated form, it dissolves much more slowly. The fact that it is made by heating barium oxide in oxygen and is composed of compact particles is accountable for this.

Every action upon a little-soluble, or slowly dissolving body, like the barium peroxide in the above actions, is rather complex. It is only the dissolved part of the substance that interacts. There is thus a physical equilibrium between the undissolved and the dissolved bodies, BaO_2 (solid) $\rightleftarrows$ BaO_2 (diss'd), the displacement of which furnishes the material for the chemical action. The latter has therefore to follow the pace set by the former. When barium sulphate is precipitated, another physical equilibrium follows the chemical change: $BaSO_4$ (diss'd) $\rightleftarrows$ $BaSO_4$ (solid). When relatively insoluble bodies are used or produced, there is thus a chain of equilibria each depending on the others:

$$BaO_2 \text{ (solid)} \leftrightarrows BaO_2 \text{ (diss'd)} + H_2SO_4 \leftrightarrows H_2O_2 + BaSO_4 \text{ (diss'd)} \leftrightarrows BaSO_4 \text{ (solid)}.$$

If the barium sulphate ceased to be precipitated, its interaction in solution with the hydrogen peroxide would drive the central action backwards, and barium peroxide would be precipitated instead. The success of the process thus depends on the fact that barium sulphate is even less soluble than barium peroxide.

When carbon dioxide is used (see above), a similar chain of equilibria exists, and in that case it is the barium carbonate that is the less soluble substance.

Other Modes of Formation. — Hydrogen peroxide is formed by the direct union of hydrogen and oxygen. When a hydrogen flame is allowed to play upon ice, appreciable amounts of the peroxide are saved from being decomposed, as they ordinarily would be by the heat of the action, and are found in the water.

It may be obtained by the action of acids upon the peroxides of calcium, strontium, zinc, and copper.

Traces of hydrogen peroxide are formed when zinc, copper, lead, and other metals are shaken with air and dilute sulphuric acid. It is produced when oxygen is passed, in the neighborhood of the negative electrode, through the liquid in an electrolytic cell containing dilute sulphuric acid. The gas is reduced by the hydrogen being liberated on the platinum plate.

Physical Properties. — Hydrogen peroxide is a syrupy liquid of sp. gr. 1.5. It blisters the skin, and, when diluted, has a disagreeable metallic taste. It has been frozen (m.-p. – 2°).

Chemical Properties. — Hydrogen peroxide is very unstable, and decomposes slowly even at – 20°. The dilute aqueous solution, when free from impurities, keeps fairly well. The presence of a trace of free acid increases its stability. Free alkalies and most salts assist the decomposition; hence the necessity for purifying the commercial solution. Addition of powdered metals, of manganese dioxide, and of charcoal causes effervescence even in dilute solutions, and oxygen escapes:

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

The more concentrated solutions (38 per cent) remain quiescent in a dish of polished platinum even at 60°, but the making of a slight scratch on the bottom, beneath the surface of the liquid, causes profuse liberation of oxygen along the sharp edge thus produced. The action of the catalytic agents is therefore probably mechanical.

Since the substance cannot be vaporized, even at low pressure, without some decomposition, its molar weight has been determined by the freezing-point method (p. 291). The freezing-point of a 3.3 per cent solution in water was 2.03° below that of the water itself. Hence, in 1000 g. of water, 3.3 g. would have given a depression of $2.03 \times 96.7 \div 1000$, or 0.196°. Therefore a depression of 1.89° would have been caused by $3.3 \times 1.89 \div 0.196$, or 31.8 g., which is the required molar weight. Now the formula HO corresponds to a molar weight of 17 and H_2O_2 to one of 34. It is evident, therefore, that the latter is the correct formula.

Hydrogen peroxide, in solution in water, is a feeble acid. The normal molar weight and very small electrical conductivity (see Chap. xix) show that only a very small proportion of it can be ionized. As an acid it enters into double decomposition readily. Thus, when it is added to solutions of barium and strontium hydroxides, the hydrated peroxides appear as crystalline precipitates:

$$Sr(OH)_2 + H_2O_2 \rightleftarrows 2H_2O + SrO_2.$$

The precipitation involves another equilibrium: $SrO_2 + 8H_2O \rightleftarrows SrO_2, 8H_2O$ (solid). The action of hydrogen peroxide upon chromic acid (H_2CrO_4) is probably of a similar nature. The composition of the product, which gives a beautiful blue solution, is not definitely known,

as it decomposes almost immediately. Its formation, by adding a drop of potassium dichromate to an acidulated solution of the peroxide, is used as a test for the latter. The acid interacts with the dichromate, giving the necessary chromic acid:

$$H_2SO_4 + K_2Cr_2O_7 + H_2O \rightleftarrows 2H_2CrO_4 + K_2SO_4.$$

The blue substance has the property, unusual in inorganic compounds, of dissolving much more readily in ether than in water. It is also much less unstable when removed from the foreign materials in the aqueous solution. Hence the test is rendered more delicate by extracting the solution with a small amount of ether. In the ethereal layer the color of the compound is more permanent, as well as more distinctly visible on account of the greater concentration.

Hydrogen peroxide is a much more active oxidizing agent than free oxygen. It liberates iodine from hydrogen iodide, an action which, in presence of starch emulsion (*cf.* p. 235), is used as a test for its presence:

$$2HI + H_2O_2 \rightarrow 2H_2O + I_2.$$

It converts sulphides into sulphates. The white lead (*q.v.*) used in paintings is changed by the hydrogen sulphide in the air of cities to black lead sulphide, $PbCO_3 + H_2S \rightarrow PbS + H_2O + CO_2$. This may be oxidized to white lead sulphate by means of hydrogen peroxide:

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O,$$

and in this way the original tints of the picture may be practically restored. Organic coloring matters are changed into colorless substances by an action similar to that of hypochlorous acid (*cf.* p. 269). Hence hydrogen peroxide is used for bleaching silk, feathers, hair, and ivory, which would be destroyed by the more violent agent. The products of its decomposition, being water and oxygen only, are harmless, and, on this account, it is used as a bactericide in surgery.

Hydrogen peroxide exercises the functions of a reducing agent in special cases, also. Thus, silver oxide is reduced by it to silver:

$$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2.$$

A solution of potassium permanganate, in which the permanganic acid has been set free by an acid, $KMnO_4 + H_2SO_4 \rightleftarrows HMnO_4 + KHSO_4$, is rapidly reduced. The permanganic acid, with excess of sulphuric acid, tends to undergo the first of the following changes, *provided a*

substance is present which can take possession of the oxygen that would remain as a balance:

$$2HMnO_4 + 2H_2SO_4 \rightarrow 2MnSO_4 + 3H_2O\ (+ 5O) \quad (1)$$
$$(5O) + 5H_2O_2 \rightarrow 5H_2O + 5O_2 \quad (2)$$
$$2HMnO_4 + 2H_2SO_4 + 5H_2O_2 \rightarrow 2MnSO_4 + 8H_2O + 5O_2$$

The first partial equation has been doubled to secure the even number of units of hydrogen required for the formula of water.

In all reductions by hydrogen peroxide, each molecule of the latter removes but one atomic weight of oxygen. Whether it behaves thus because its two hydrogen units combine with *this* oxygen and *all its own* oxygen escapes, or because it furnishes water and *one* oxygen unit of the pair required to form the molecule of free oxygen (the substance reduced furnishing the other), has not been determined.

The above action is used in quantitative analysis for estimating the quantity of hydrogen peroxide in a given liquid after the liquid has been acidified. The amount of a standard (p. 236) solution of the permanganate which is required to decompose all the peroxide is measured by means of a burette (*q.v.*). The permanganate is deep reddish-purple in color, while the products are colorless. Hence, after the peroxide is exhausted, the next drop of the permanganate confers a distinct, permanent, pink tinge upon the liquid. The addition of the permanganate solution is stopped so soon as this condition is reached and the volume of it that has been used is read off.

Thermochemistry of Hydrogen Peroxide. — The formation of hydrogen peroxide from the free elements is accompanied by evolution of heat:

$$H_2 + O_2 = H_2O_2\,Aq + 45{,}300 \text{ cal.}$$

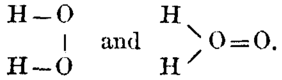
Hence the substance is formed by direct union (p. 304). But its decomposition into water and oxygen gives out a further supply of heat:

$$H_2O_2 = H_2O + O + 23{,}100 \text{ cal.}$$

The sum of these two stages, of course, yields the same result (*cf.* p. 78) as the direct formation of water (68,400 cal.).

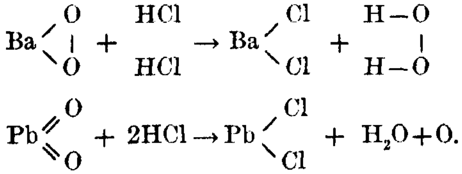
When hydrogen peroxide is used, instead of free oxygen, for oxidizing purposes, each such action liberates 23,100 calories of heat more in the former case than it would in the latter. Hence the activity of the substance as an oxidizer (*cf.* p. 271).

Peroxides: Chemical Constitution and Molecular Structure. — To represent the chemical behavior of hydrogen peroxide, two different graphic formulæ (*cf.* p. 279) have been proposed:



In the latter of the two formulæ, one of the oxygen units holds four equivalents of other materials instead of two. Oxygen being ordinarily bivalent, the two extra valences may plausibly be supposed to involve a feebler state of combination, and therefore to portray the tendency of the compound easily to give up one unit of oxygen. The *linking* of the oxygen units, common to both formulæ, expresses the fact that we do not obtain hydrogen peroxide from substances containing less than two units of this element in each mole. Thus, to be consistent, we write Na_2O_2, although we have no means of determining the molecular weight of this particular peroxide. The former of the above formulæ is more generally used.

All oxides containing two units of oxygen do not yield hydrogen peroxide, however. Thus, lead dioxide (PbO_2) gives, by interaction with dilute acids, water and oxygen only. Carrying out our system, therefore, we make barium and hydrogen peroxides alike, and we assign different constitutions (p. 224) to barium and lead dioxides and different structures to their molecules:



In confirmation of this we find that lead can form an unstable tetrachloride and other compounds in which, as in $Pb^{IV}O_2$, it is quadrivalent. But barium gives no other compounds in which there is even the semblance of quadrivalence. So our structural formula ingeniously leaves it bivalent even in BaO_2. We assign, therefore, to all substances which give hydrogen peroxide, and are therefore true peroxides, the "peroxide structure," consisting of linked oxygen units, while for those which give no hydrogen peroxide, we write formulæ in which the oxygen units are independent of one another.

Exercises. — 1. What volume of ozone will be taken up by 100 c.c. of water at 12° from a stream of oxygen containing 7.5 per cent of ozone (p. 155)?

2. Formulate the action of carbon dioxide on barium dioxide (p. 303) after the manner of that of sulphuric acid on the same substance (p. 304). The dissolving gas gives an additional equilibrium: CO_2 (gas) + $H_2O \rightleftarrows H_2CO_3$ (diss'd).

3. At what temperature will a ten per cent solution of hydrogen peroxide freeze (p. 305)?

4. Write the thermochemical equations for oxidation of indigo by ozone (pp. 271, 302) and by hydrogen peroxide.

CHAPTER XIX

ELECTROLYSIS

Introductory. — Experiment shows that most solutions which exhibit chemical transformations by interchange of groups (p. 283), and all which show evidence of dissociation by measurements of osmotic pressure, freezing-point depression, and boiling-point elevation, are precisely those which are conductors of electricity and suffer decomposition by the passage of the electric current. Solutions which, on the contrary, behave normally in respect to the three physical properties are nonconductors. Solutions of the former kind, consisting of ionogens (p. 296) dissolved, usually, in water, are called **electrolytes**, and the effect of an electric current upon them is named **electrolysis**. Solutions of the same substances in toluene, chloroform, etc., do not conduct electricity, are not decomposed by the current, and, as we have seen (p. 294), show no evidence of ionization. Substances like sugar, methyl acetate, etc., which show no evidence of dissociation, are nonconductors, whatever solvent we employ.

In endeavoring to connect these important facts, we must remember that the pure solvent by itself, and the pure substances which we dissolve in the solvent by themselves are, at ordinary temperatures, all but complete nonconductors of electricity. Dry salts, except when at high temperatures and fused, and dry hydrogen chloride (p. 182), on the one hand, and pure water (p. 95) on the other, do not permit the passage of the current. Yet a mixture of one of the former with the latter conducts extremely well. Let us consider first the nature of the decomposition which accompanies the conduction.

Chemical Changes Connected with Electrolysis. — When the wires from a battery are attached to platinum plates immersed in any electrolyte (*e.g.* Fig. 65, p. 169), we observe that the products appearing at the two electrodes are always different. They may be of several kinds physically, and will be secured for examination variously according to their nature. When they are gases which are not too soluble, they may be collected in inverted tubes filled with the solu-

tion. Solids, if insoluble in the liquid, will either remain attached to the electrode or fall to the bottom of the vessel as precipitates. Soluble substances on the other hand will usually not be visible. They may be handled by interposing a porous partition of some description which will restrain the diffusion of the dissolved body away from the neighborhood of the electrode, while not interfering appreciably with the passage of the current. Surrounding one electrode with a porous battery jar is a convenient method for effecting this.

When a current of electricity is passed in this fashion through a solution of silver nitrate $AgNO_3$, we observe that at the negative electrode metallic silver is set free and adheres to the plate. At the positive electrode a gas, oxygen, appears. Since these substances do not account for all the constituents of the salt, we are impelled to examine the solution around each pole, and discover that nitric acid (HNO_3) is being formed along with the oxygen at the positive end. Although we have *now* found something *more* than the two parts of the original molecule, we have little difficulty in explaining the presence of these two products on the assumption that the original molecules were divided into the parts, Ag and NO_3. The latter, since it is not a known compound, must have interacted with the water to produce nitric acid and oxygen: $2NO_3 + H_2O \rightarrow 2HNO_3 + O$. The atomic oxygen has subsequently united so as to form the gas (O_2). The whole change may therefore be tabulated as follows:

$$\text{Neg. Wire, Ag.} \longleftarrow \text{Ag.NO}_3 \longrightarrow O_2 \text{ and } HNO_3\text{, Pos. Wire.}$$

If we substitute cupric nitrate $Cu(NO_3)_2$, we obtain a red deposit of metallic copper on the negative plate, and at the positive plate oxygen and nitric acid are formed. We infer therefore that the parts of the original molecule are Cu and NO_3:

$$\text{Neg. Wire, Cu} \longleftarrow \text{Cu.}(NO_3)_2 \longrightarrow O_2 \text{ and } HNO_3\text{, Pos. Wire.}$$

With a solution of potassium nitrate we find hydrogen and oxygen appearing at the negative and positive electrodes respectively. Litmus paper, however, shows the presence in the solution of a base (potassium hydroxide, KOH) at the negative and an acid (nitric acid) at the positive end. Secondary chemical changes have occurred at both poles. We infer that the parts of the parent molecules are K and NO_3. The former, in its customary manner (p. 99), instead of being liberated, gave rise to free hydrogen and potassium hydroxide,

$2K + 2H_2O \rightarrow 2KOH + H_2$:

Neg. Wire, H_2 and KOH $\longleftarrow$ $K.NO_3$ $\longrightarrow$ O_2 and HNO_3, Pos. Wire.

We are confirmed in these conclusions when we employ a pool of mercury in place of the negative wire. A portion of the potassium is found to have dissolved in the mercury and escaped interaction with the water.

When dilute sulphuric acid is electrolyzed (p. 95), the result is a liberation of hydrogen and oxygen and an accumulation of sulphuric acid round the positive electrode:

Neg. Wire, H_2 $\longleftarrow$ $H_2.SO_4$ $\longrightarrow$ O_2 and H_2SO_4, Pos. Wire.

All acids give hydrogen alone at the negative electrode.

Of the various illustrations we have encountered, the electrolysis of hydrochloric acid (p. 184) happens to be the only one which delivers the two components (H and Cl) with the minimum of modification by secondary interaction. The gases liberated are, of course, H_2 and Cl_2. The chlorides, bromides, and iodides of all such metals as do not interact with water give equally simple results. Secondary actions are equally worthy of notice, not only because they are common, but also because they often play a part in industrial electrolytic processes.

On now comparing the chemical behavior of a large number of ionogens with the results of electrolysis of the same substances, we are led to identical conclusions. Acids contain hydrogen possessing certain special properties (p. 281), and by electrolysis they divide so as to give up *this constituent alone* at one electrode. Salts undergo double decomposition easily and exchange radicals with other ionogens (p. 283), and the current divides their molecules at the *same point*, liberating the radicals.

Quite a crop of problems is raised by this discovery: Since a solution may eventually be cleared of all the hydrochloric acid, for example, which it contains, we should like to know how the constituents in the center of the cell reach the electrodes. Then there is the question of the quantity of electricity required to effect a given amount of decomposition in a given ionogen. Finally, since the details are, as usual, inscrutable, a formulative hypothesis will be needed to explain the whole proceeding.

Ionic Migration. — The first of these questions is easily answered by experiment. We have only to take an ionogen one of whose radi-

cals is colored, and watch the movement of the colored material as it drifts towards the electrode. Thus, in dilute cupric sulphate solution, a freezing-point determination shows that the depression has practically double the normal value. In other words, the dissociation

$$CuSO_4 \rightleftarrows Cu^{\cdot\cdot} + SO_4''$$

is almost complete.* Now, the blue color of this solution cannot be due to the remaining molecules of $CuSO_4$, for anhydrous cupric sulphate is colorless. Nor is it due to the color of the SO_4'' ion, for dilute potassium sulphate and dilute sulphuric acid are both colorless. On the other hand, all cupric salts, in dilute solution, have the same tint. The color is therefore that of the cupric ion ($Cu^{\cdot\cdot}$). Similarly the deep-yellow tint of potassium dichromate $K_2Cr_2O_7$ (*q.v.*) is that of the Cr_2O_7'' ion. Hence either of these substances will serve the purpose of showing how the ionic material moves.

One of the above salts is dissolved in warm water containing about 5 per cent of agar-agar, and the lower part of the U-tube (Fig. 77) is charged with the mixture. After this fluid has set to a jelly, a few grains of powdered charcoal are added on each side to mark the present limits of the colored ions, or strips of paper are pasted on the outside. Then any colorless electrolyte, such as potassium nitrate solution, is added on each side, and the electrodes are hung one in each limb. The lower half of the potassium nitrate solution on each side contains agar-agar also. The agar-agar does not offer any appreciable resistance to the motion of the ions, and is presumed to form a sort of open network in the solution. It is added to prevent all motion of the water. Immersion of the whole tube in ice and water prevents the melting of the jelly by the heat generated by the current.

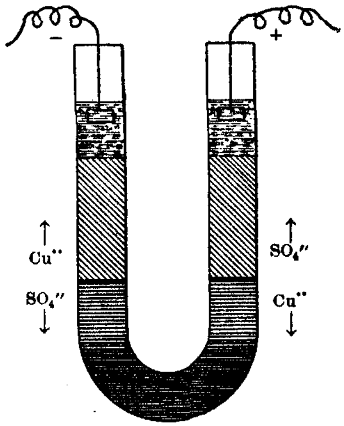


FIG. 77.

* In all ions the valence is indicated, as in this equation, by the number of superior marks · or ′ as the case may be. The use of this custom will appear presently.

After a time, we observe that the blue cupric ions ascend above the mark on the negative and descend away from it on the positive side. With potassium dichromate the yellow ions move in the opposite direction with reference to the poles. In each case there is no shading off in the tint. The motion of the whole aggregate of colored ions occurs in such a way that, if the contents of the tube were not held in place by the jelly, we should believe that a gradual motion of the whole solution was being observed. With a current of 110 volts, and a 16-candle power lamp in series with the cell, the effect becomes apparent in a few minutes.

Although the SO_4'' ions are invisible, we may safely infer that they are drifting towards the positive electrode. Indeed, this can be demonstrated by interposing a shallow layer of jelly containing some barium salt a little distance above the charcoal layer on the positive side. When the SO_4'' ions reach this, barium sulphate begins to be precipitated and the layer becomes cloudy. In a similar way the progress of other colorless ions may be rendered visible.

It appears therefore that electrolysis is not a local phenomenon, going on round the electrodes only, but that the whole of the dissociated solute is set in motion. It is on account of this remarkable property of traveling or **migrating** towards one or other of the electrodes connected with a battery that the ions receive their name (Gk. ἰών, going). The term was first applied by Faraday to the materials liberated round the electrodes.

Relative Speed of Migration of Different Ions. — The speeds of different ions may readily be compared. The cupric ion moves at the same speed whatever salt of copper we employ. In fact, the speeds of all ions are individual properties and are independent of the nature of other ions that may be present. The speeds of all are increased by using a current of greater electromotive force. Under similar conditions, the relative speeds of most ions are in the neighborhood of 50 or 60, on the scale commonly used in expressing ionic velocities. Thus, we have, $K^{\cdot}$ 65.3, Cl' 65.9, $Cu^{\cdot\cdot}$ 49. The speed of the hydrogen ion is the greatest of all, 318, while that of hydroxyl ion (OH') comes next, being 174.

The actual speeds of these ions in dilute solutions at 18°, when driven by a potential difference of 1 volt between plates 1 cm. apart, expressed in cm. per hour is: $K^{\cdot}$ 2:05, Cl' 2.12, $Cu^{\cdot\cdot}$ 1.6, $H^{\cdot}$ 10.8, OH' 5.6.

By an experiment similar to the last, and devised by A. A. Noyes, the relative speeds of different ions may be demonstrated. The U-tube (Fig. 78, showing the same tube *A* before the current starts, and *B* after it has been passing for some time) is partly filled with agar-agar emulsion containing potassium chloride and phenolphthalëin (see Indicators). On the right side, a few drops of potassium hydroxide have been added to render the mixture pink. On the left, a few drops of hydrochloric acid are present, and the mixture is colorless. Above the charcoal layer, in the right limb, a mixture of hydrochloric acid and cupric chloride (*i.e.*, $H^{\cdot}$ and $Cu^{\cdot\cdot}$), and in the left limb potassium hydroxide solution (*i.e.* OH'), are placed. The positive electrode is introduced on the right and the negative on the left. The $H^{\cdot}$ and $Cu^{\cdot\cdot}$ ions drift away from the former down the tube towards the

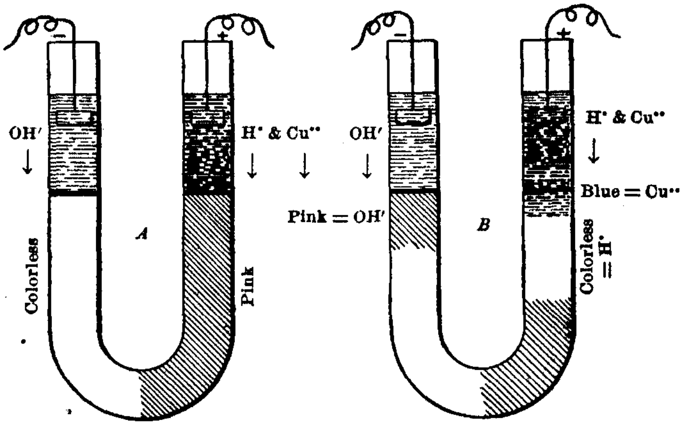


FIG. 78.

latter, the OH' ions away from the latter down the tube towards the former. The motion of the $H^{\cdot}$ is marked by the disappearance of the pink color, that of the $Cu^{\cdot\cdot}$ by the advance of a blue layer, that of the OH' by the progress of a pink coloration.* By the time the $H^{\cdot}$ ions have been displaced 5½ cm., the $Cu^{\cdot\cdot}$ ions have moved 1 cm. and the OH' about 2½ cm. These distances indicate their relative speeds of migration.

Faraday's Laws. — Having learned that electrolytes furnish at least *two* definite decomposition products by the action of the electricity, we naturally inquire next whether there is any chemical relation between the quantities of the products set free by the same current. Quantitative experiments in electrolysis show the most perfect adjustment in this respect. Thus, in a single cell, the quantities of material

* Bases, on account of the OH' they give, turn phenolphthalëin solutions from colorless to pink; acids, on account of the $H^{\cdot}$ they furnish, turn it from pink to colorless (see Indicators).

liberated at the two poles are invariably chemical equivalents of one another. With hydrochloric acid, while 1.008 g. of hydrogen is being liberated at one pole, 35.45 g. of chlorine are set free in the same time at the other. While 63.6 g. of copper are being deposited from cupric sulphate at one pole, 96 g. of SO_4 are being liberated at the other, and, by interaction with the water, form 16 g. of oxygen and 98 g. of sulphuric acid.

Again, **the amount of any one substance liberated is proportional to the quantity of electricity which has traversed the cell.** This is the **first part of Faraday's law.**

Finally, the passage of equal quantities of electricity through several different acids liberates equal amounts of hydrogen from each. This is true, whether the passage of the given quantity of electricity is compressed into a brief time in one case and spread over a longer time in another, or is uniform in all cases compared. It is irrespective of the state of dilution and of the temperature of each acid. Thus two moles of hydrochloric acid are always decomposed for every one of sulphuric acid by the same current. Similarly, if in different cells we place solutions of substances like sodium chloride (NaCl), cupric chloride ($CuCl_2$), antimony chloride ($SbCl_3$), ferrous chloride ($FeCl_2$), and ferric chloride ($FeCl_3$), equal amounts of chlorine are liberated by currents of equal strength in the same time in each.

If we consider the relation of these facts to the equivalence of the materials liberated in any one cell, it will be evident that when one gram of hydrogen is liberated from each of the two acids mentioned above, one equivalent of chlorine will be set free in the one cell, and one equivalent of SO^4, or half the weight represented by the formula, will be set free in the other. Similarly, with the chlorides of the first three metals, while 35.45 g. of chlorine are being liberated in each cell, the quantities of the metal set free will be, of sodium 23 g., of copper one-half of 63.6 g., and of antimony one-third of 122 g. Finally, with the two iron salts, the quantities of iron liberated by the same current will be one-half and one-third of 56 grams respectively.

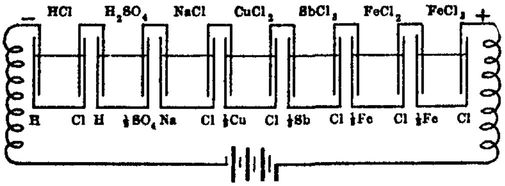


FIG. 79.

The simplest way in which to insure the passage of precisely equal

amounts of electricity through all the cells is to arrange them in series. We know that in such circumstances the quantity of electricity traversing any section of the whole circuit must be the same as that traversing any other. In a series of cells containing substances like the above, therefore, during the time that 1.008 g. of hydrogen is being set free, we shall have liberation of the equivalent quantities of each of the other ions (Fig. 79). Thus the **second part of Faraday's law** states that **chemically equivalent quantities of ions are liberated by the passage of equal quantities of electricity.**

The Ionic Hypothesis. — The main facts in regard to electrolytic conduction being now before us, the problem is to adapt the atomic and molecular hypotheses to their explanation, that is, to their detailed description. There are two peculiarities to be accounted for:

How can the production of a conducting medium by mixing two nonconductors be imagined to take place? The solvent is a nonconductor, and the ions, even if they are composed of conducting material, are distributed through the liquid as independent particles and cannot furnish a continuous medium for the stream of electricity. This will be clear when we remember that although liquid mercury is an excellent conductor, mercury vapor, composed as it is of conducting particles, is not a conductor.

Again, the conducting power of the solution is indissolubly connected with the fact that the original molecules of the solute have been broken up by the solvent into smaller molecules containing one or more atoms. Why should this particular kind of sub-molecules be attracted by electrically charged plates, which have been lowered into the solution, when molecules of dissolved sugar, for example, are not so attracted?

An answer to the second question readily suggests itself. The only bodies which we find to be conspicuously attracted by electrically charged objects are bodies which are *already provided with electric charges of their own.* Thus we are led to add to the molecular hypothesis the assumption that substances which undergo dissociation in solution **divide themselves into** a special kind of **electrically charged molecules.** Since the solution, as a whole, has itself no charge, equal quantities of positive and negative electricity must be produced:

$$HCl \rightleftarrows \overset{+}{H} + \overset{-}{Cl} \quad NaCl \rightleftarrows \overset{+}{Na} + \overset{-}{Cl} \quad NaOH \rightleftarrows \overset{+}{Na} + \overset{-}{OH}.$$

Wild as this supposition seems at first sight to be, it turns out that

no valid objection to it can be raised. That it furnishes an answer to both of our questions must first be shown.

A battery is a machine which maintains two points, its poles, or two wires connected with them, at a constant difference of potential. One cell of a storage battery, for example, maintains a potential difference of two volts. When the wires are joined, directly or indirectly, the poles are immediately discharged, but the cell continuously reproduces the difference in potential by generating fresh electricity. Now the effect of immersing two plates, one of which is kept by the battery at a definite positive potential and the other at a definite negative potential, into a liquid filled with floating multitudes of minute bodies, *already highly charged,* may easily be foreseen.

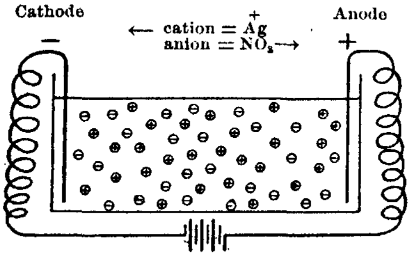


FIG. 80.

The figure (Fig. 80) will convey some idea of the behavior of the parts of a system such as we have imagined. The electrodes are marked — and +. The negatively charged plate attracts all the positively charged particles in the vessel, and, although these particles are in continuous and irregular motion, they nevertheless begin, on the whole, to drift toward the plate in question. On the other hand, the negatively charged particles are repelled by this plate and attracted by the positive plate, so that they drift in the opposite direction. Those which are nearest each plate, on coming in contact with it, will lose their charges of electricity, turning thereby into the ordinary free forms of the matter of which they are composed. The continuous removal of the electrical charges of the plates through contact with ions of the opposite charge furnishes occasion for recharging of the plate from the battery, and thus gives rise to a continuous current in each wire. Again, the continuous drifting of positively and negatively charged particles in opposite directions through the liquid, constitutes what, in the view of all external means of observation, appears to be an electrical current also. A magnetized needle, for example, which is deflected when brought near one of the wires of the battery, is influenced in the same way by being brought over the liquid between the electrodes. The illusion, so to speak, of an electric *current* is complete, although in reality it is a *convection* of electricity that is taking place. Further-

more, the quantity of electricity being transported across any section of the whole system is the same as that across any other, whether this section be taken through one of the wires, through the electrolyte, or even through the battery at any point. As fast as the ions are thus annihilated as such, the undissociated molecules are drawn upon for the production of fresh ones, as in all chemical equilibria. Eventually, by continuing the process long enough, if the substances set free are actually deposited and do not go into solution again in any form, the liquid can be entirely deprived of the solute which it contains.

The analogy to the transportation of a fluid like water is noticeable, although not complete. Water may be transported in three ways. It may flow through a pipe, it may pass by pouring freely from one container to another, and it may be carried in vessels. Thus a stream of water, essentially continuous, might be arranged, in which part of the passage took place through the pipes, part by pouring from the pipes into buckets, and part by the carrying of those buckets between the ends of the pipes. The quantity of water passing a given point per minute in this system would be the same at every part, although the actual method by which the water was transported past the various points might be different. In such a disjointed circuit we suppose the electricity to move when carried from a battery through an electrolytic cell. It flows in the wire, passes by discharge between the pole and the ion, and is transported upon the ions in the liquid. The parallel is imperfect, however, because we have used the conception of *two* electric fluids and *because the ions are already charged in the solution, and before any connection with the battery is made.* They do not, so to speak, transport the electricity of the battery, but their own.

Difficulties Presented by this Hypothesis. — The question was raised (p. 295), as to how we can imagine separate atoms of sodium to exist in water without acting upon it, as the metal sodium usually does. But the ions of sodium in sodium chloride solution are *not* metallic sodium. They bear large charges of electricity. They possess an entirely different, and in fact, by measurement, much smaller amount of chemical energy than free sodium. And, as we have seen, the properties of a substance are determined as much by the energy it contains as by the kind of matter. Metallic sodium and ionic sodium are, simply, different substances.

We think of hydrogen chloride and common salt as exceedingly stable substances, and are averse to believing that precisely these com-

pounds should be highly dissociated by mere solution in water. But it must be remembered that in solution they undergo chemical change very easily, and it is only in the dry form that they show unusual stability.

Again, why do not the ions combine in response to the attractions of their charges? The answer is that they do combine, but the rate at which combination takes place is no greater than that at which the molecules decompose, so that on the whole the proportion of ions to molecules remains unchanged.

Finally, it might appear that the assumption that bodies could retain high charges in the midst of water is contrary to all experience. It must be remembered, however, that the molecular, pure water, which separates the ions from one another, is a perfect nonconductor. The moisture which covers electrical apparatus and causes leakage of static electricity is not pure water, but a dilute solution containing carbonic acid (p. 114) and materials from the glass of which the apparatus is made. It conducts away the charge electrolytically, by means of the ions it contains, and not by itself acting as a conductor.

Amounts of Electricity on the Ions. — Since one atomic weight of chlorine (35.45 parts) and one atomic weight of hydrogen (1.008 parts) are simultaneously liberated in the electrolysis of hydrochloric acid and the solution remains electrically neutral, it follows that the ions of hydrogen and chlorine bear equal charges. Again, since the same thing is true of one atomic weight of copper (63.6 parts) and two atomic weights of chlorine (70.9 parts) in cupric chloride, it follows that the cupric ion bears a double charge. Similarly, the antimony (p. 316) ions bear triple charges. In ferrous and ferric salts the amounts carried by the iron ions differ, being in the one case twice, and in the other three times as great as those carried by the hydrogen or chlorine ions. We may sum this up, then, by saying that **univalent ions possess the same quantity of electricity, and other ions bear quantities greater than this, in proportion to their valence.** This rule is simply a restatement of Faraday's law, which it brings into direct relation to the ionic hypothesis.

In writing equations involving ions, the numbers of + and − charges must always be equal:

$$KCl \rightleftarrows \overset{+}{K} + \overset{-}{Cl} \qquad SbCl_3 \rightleftarrows \overset{+++}{Sb} + 3\overset{-}{Cl}$$

$$CuCl_2 \rightleftarrows \overset{++}{Cu} + 2\overset{-}{Cl} \qquad FeCl_2 \rightleftarrows \overset{++}{Fe} + 2\overset{-}{Cl}$$

$$CuSO_4 \rightleftarrows \overset{++}{Cu} + \overset{=}{SO_4} \qquad FeCl_3 \rightleftarrows \overset{+++}{Fe} + 3\overset{-}{Cl}$$

In order that this idea may be carried out consistently, the liberation of any of these ionic materials at one electrode in electrolysis is written as follows:

$$\overset{+}{K} + \ominus \rightarrow K \qquad 2\overset{-}{Cl} + 2\oplus \rightarrow Cl_2.$$

Here $\ominus$ and $\oplus$ represent the unit quantities of negative and positive electricity furnished by the battery to the electrodes and destroyed by opposite charges upon the ions.

The harmony between the quantity of electricity and the chemical valence of the material which it liberates is complete. The picture which the process of electrolysis in a series of cells (p. 316) presents to our minds is very interesting. The progress of the electricity through the series is accompanied by a simultaneous discharge in all the cells of chemically corresponding numbers of atoms. For every atom of antimony that is liberated in one cell, three atoms of chlorine, three atoms of hydrogen, and one atom of ferric iron, are set free at the same time. For two atoms of ferric iron, three atoms of ferrous iron and three atoms of copper are deposited. Even in the *battery* which generates the current, the chemical changes taking place proceed atom for atom and valence for valence in unison with those in the cells on the circuit. For example, if the battery contains zinc plates, for every atom of zinc that dissolves, one of copper and two of chlorine will be liberated in one of the cells. Our imaginary mechanism thus puts all the processes going on in the circuit in the light of movements of the parts of a perfectly adjusted and interlocked machine.

Résumé and Nomenclature. — An **ion** may be defined as, an atom or group of atoms bearing a positive or negative charge of electricity, and formed through the dissociation of an ionogen by a solvent like water.

Each molecule gives two kinds of ions with opposite charges. These two are forthwith distinct and independent substances, save that the attractions of the charges prevent separation by diffusion. They differ from non-ionic substances of the same material composition when such are known. The electrical charge is one of the essential constituents, and when it is removed the properties alter entirely. Thus we have two kinds of hydrogen, gaseous molecular hydrogen (H_2), and ionic hydrogen ($\overset{+}{H}$), with entirely different chemical properties (p. 295).

Since the writing of the + and − charges over the symbols

occupies much space, we shall hereafter employ a dot for the former and a little dash for the latter: $H^{\cdot}$, Cl', $Cu^{\cdot\cdot}$, SO_4'', $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $NH_4^{\cdot}$. In the ions formed from one molecule, the number of dots and dashes must be equal.

Since ionic hydrogen, ionic chlorine, etc., are entirely different in physical and chemical properties from the corresponding free elements, they should receive separate names. When it is inconvenient to say "ionic hydrogen," "nitrate ions" (NO_3'), etc., the following, based on Walker's system, will be used:

Symbol.	Name.	Anion of	Symbol.	Name.	Cation of Salts of
SO_4''	Sulphanion	Sulphates	$Na^{\cdot}$	Natrion	Sodium
SO_3''	Sulphosion	Sulphites	$Ca^{\cdot\cdot}$	Calcion	Calcium
ClO_4'	Perchloranion	Perchlorates	$Cu^{\cdot\cdot}$	Dicuprion	Cupric copper
ClO_3'	Chloranion	Chlorates	$K^{\cdot}$	Kalion	Potassium
Cl'	Chloridion	Chlorides	$Fe^{\cdot\cdot\cdot}$	Triferrion	Ferric iron
S''	Sulphidion	Sulphides	$NH_4^{\cdot}$	Ammonion	Ammonium
NO_3'	Nitranion	Nitrates	$Fe^{\cdot\cdot}$	Diferrion	Ferrous iron
OH'	Hydroxidion	Hydroxides (bases)	$H^{\cdot}$	Hydrion	Hydrogen(acids)

Faraday distinguished the two kinds of material which proceed with and against the positive current by name. His terminology is still used. Ions which proceed in the same direction as the positive current are called **cations** (Gk. κατά, down). Such are $H^{\cdot}$, $Cu^{\cdot\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$. They are **metallic elements**, or groups which play the part of a metal. The electrode (Gk. ὁδός, a path) upon which they are deposited, the negative electrode, is spoken of as the **cathode** (Gk. ἡ κάθοδος, the way down).

The particles which move in the direction of the negative current, and against that of the positive, are named **anions** (Gk. ἀνά, up). The ions Cl', NO_3', SO_4'', MnO_4' are of this kind. They are usually composed of **non-metals**, although sometimes, as in MnO_4', the components may be partially metallic. *They are set free at the positive electrode*, which is therefore named the **anode** (Gk. ἡ ἄνοδος, the way up). Chemists speak of metals and non-metals as **positive** and **negative elements**, respectively (*cf.* p. 119), even when electrical relations are not directly in question, and ions are not concerned.

Actual Quantities of Electricity Concerned in Electrolysis.— The **coulomb** is the unit quantity of electricity: the liberation of one

gram of hydrogen corresponds to the passage of 96,540 coulombs round the circuit. In other words, one gram of hydrion ($H^{\cdot}$) carries this quantity of electricity. Equivalent amounts of other ions, for example, 108 g. of argention ($Ag^{\cdot}$) and $\frac{96}{2}$ g. of sulphanion (SO_4''), carry the same quantity. Thus the unit quantity of electricity, one coulomb, deposits, or is carried by $\frac{1}{96540}$ g. of hydrogen or $\frac{108}{96540}$ g. of silver.

In consequence of this, the deposition of silver or copper is used as a means of measuring quantities of electricity. The increase in weight of the negative electrode in a cell, called under such circumstances a **voltameter**, is a measure of the quantity of electricity which passes around the whole circuit of which it forms a part.

It is more common to define the quantity of electricity in terms of **current strength**. A current of such nature that one coulomb flows through the system per second is said to have a strength of one **ampere**. Such a current liberates $\frac{1}{96540}$ g. of hydrogen or $\frac{108}{96540}$ g. of silver per second. A current which deposits twice as much, has two amperes current strength.

From this it is evident that a current of one ampere would take 96,540 seconds, or twenty-six hours and 49 minutes, to deposit 1 g. of hydrogen (about 11 liters), or 108 g. of silver, or 48 g. of sulphanion. A current of five amperes would accomplish the same result in a fifth of the time.

The Electrical Energy Required to Decompose Different Compounds. — Chemical compounds are of very different degrees of stability, and hence the quantities of energy, electrical or otherwise, required to decompose them vary widely. Thus, hydrogen chloride is very stable, while hydrogen iodide is easily decomposed by heating. The disunion of equivalent quantities of these substances in aqueous solution absorbs 39,300 cal. and 13,100 cal. of heat energy, respectively. Hence, although equal quantities of electricity (96,540 coulombs in each case) perform this office, very unequal amounts of electrical energy are used up in the electrolysis.

The energy in a stream of water is represented by the product of the quantity passing a given section and the pressure or head of water available at that point. If the pressure is low, the work that can be done will be small, even if the quantity flowing is great. So electrical energy is expressed by the product of the current strength, or quantity passing per second during a certain period of time, and the electro-

motive force. The latter corresponds to pressure, and is defined by the difference in potential of two points in the circuit between which the energy is being used up.

Now, in the series of cells which was described (p. 316), each cell, while being traversed by the same quantity of electricity as any of the others, cuts down the electromotive force of the current in proportion to the amount of energy consumed by the decomposition going on within it. Hence, while a voltmeter will show no difference in potential between two neighboring parts of the heavy wires used as connections, for no work is being done in the wires, it will show a considerable difference in potential between two points which are separated by one of the cells.

A system of cars hauled by a cable is analogous to our set of cells and more familiar. When clutched to the cable, all the cars move with equal speed, but, being loaded with different numbers of passengers, take very different amounts of power from the moving cable.

We should infer from this, that to decompose every electrolyte, a current of a certain minimum electromotive force, sufficient to furnish the fall in potential necessitated by the chemical change, which would be different in different cases, would be required. This is found to be the case. For the easy decomposition of sulphuric acid and liberation of the products an electromotive force of at least 1.92 volts is necessary, for hydrochloric acid 1.41 volts, for hydriodic acid 0.53 volts, for zinc sulphate 2.7 volts, and for silver nitrate 0.70 volts. When we use a current of electromotive force falling short of that specified, we find that the flow of electricity is interrupted. The electrolytic cell practically forms a break in the circuit. (see Chap. xxxviii).

Polarization. — It is found that when plates of platinum, a metal which is not acted upon by the liberated radicals, are used, the products of electrolysis accumulate on the electrodes and tend to produce a reverse current (see Electromotive chemistry). The cell is said to be **polarized**. Thus, after hydrochloric acid has been electrolyzed for a few moments, hydrogen and chlorine adhering to the two platinum plates set up this current.* If the battery is disconnected, the electrolytic cell becomes for a brief time itself a battery, the re-ionization of the hydrogen and chlorine (reproducing hydrochloric acid) furnishing the energy. It is the continuous overcoming of this reverse current,

* If copper plates are used, cupric chloride is formed at the positive plate (anode), and no polarization can occur at that plate.

and prevention of the reunion, that demands the minimum electromotive force (here 1.41 volts) of which mention has just been made.

It is possible to arrange cells in which no polarization can take place. Thus, when we electrolyze cupric sulphate between *copper* electrodes, the copper is deposited upon one plate and the SO_4 removes the copper from the other plate, forming cupric sulphate, thus restoring the electrolyte to its original condition. The only difference is that a portion of the copper has been deposited on one pole and an equivalent amount has been removed from the other (see Copper refining). With such cells, no minimum difference in potential is required to effect electrolysis, for there is no polarization current to be overcome. The feeblest electric current will produce continuous, if slow, chemical change.

This result is extremely interesting, for it shows that the operation of electrolysis in itself does not require the consumption of much energy. If the molecules were actually torn apart by the electricity, then all electrolytic operations would require a minimum electromotive force for their maintenance. The fact just stated, therefore, is significant, for it confirms the present views in regard to the theory of solutions. It is in agreement with the belief that the actual production of the ions is accomplished by the water in advance, and quite independently of the use of electricity, and that the sole function of the electricity in the process of electrolysis *within the solution* consists in the pilotage of the ions in reverse directions according to their charges, an operation which necessarily consumes but little energy. The friction alone of the moving ions has to be overcome. It makes clear the fact that it is only when the chemical change in the cell involves the actual decomposition of some material, accompanied (as in the electrolysis of hydrochloric acid) by the final delivery of the constituents in the free state, that considerable consumption of electrical energy, proportional to the extent of the chemical change, must take place.

Conductivity for Electricity. — The facility with which equimolar solutions of different substances conduct electricity, when they are placed under like conditions, depends jointly on the degree of ionization, on the speed with which the ions move, and on the valence of the ions. When equivalent instead of equimolar amounts are compared, the last of these factors drops out of consideration. The most highly dissociated acids, as we should expect, since they give large numbers of the speedy hydrogen ions, are the best conductors. The

highly ionized bases, such as potassium and sodium hydroxide, come next. The best conductors among salts fall considerably behind both of these, because, although their degrees of ionization may not be less than those of the best conducting acids and bases, their ions all move more slowly than do hydrion and hydroxidion. On the other hand, concentrated solutions all conduct badly, relatively to the number of molecules originally used in making them, because only that proportion of the substance which is ionized contributes to the conduction (p. 318). All this is just what we should expect, in view of our hypothesis, for the passage of the electricity must be dependent upon the frequency with which discharges of the ions upon the electrodes occur, and this, in turn, must depend upon both the concentration and the speed of the ions. To return to an analogy used once before, the rate at which a fluid can be transferred between two reservoirs must depend upon the denseness of the array of buckets available and on the speed with which they are moved and on their individual capacity.

Ordinarily, it is the resistance which a substance presents to the passage of the electric current which is measured. Obviously, however, for the present purpose it is more convenient to give expression to the reciprocal of this value, which we term the **conductivity**. In order that the results may have chemical significance, we express them in terms of the conducting power of one gram-equivalent of the compound dissolved in water and placed in a narrow cell whose opposite walls, of great area and situated one centimeter apart, form the electrodes. Since the water is a nonconductor, the conducting power of the solution intervening between the plates is a measure of the capacity of the dissolved substance for facilitating the discharge between the poles. Inasmuch as varying the amount of the solvent will not affect the velocity of the ions of the substance, any alteration in conducting power resulting from dilution must depend solely on the change in the number of ions available for carrying off the electricity. The conductivities of solutions of the same substance in different concentrations must therefore be proportional to the degrees of its ionization.

A trough and amperemeter * (Fig. 81) may be used to illustrate this principle. The electrodes are here long strips of copper foil, which pass down at the ends of the trough and are situated, not one centimeter, but ten or fifteen centimeters apart, in order that the con-

* For these experiments an amperemeter of low resistance, 0.5–1 ohm, must be used, and a battery of one or two accumulator cells is sufficient.

tents of the vessel may be more easily seen. When the two instruments are placed in circuit with a battery and very pure water is poured into the cell, the amperemeter does not indicate the passage of any current of electricity. When a shallow layer of concentrated hydrochloric acid is substituted, the situation is that a definite amount of hydrogen chloride dissolved in a small amount of water forms one of the links in the electric circuit. The deflection of the needle in the amperemeter indicates that a certain current of electricity is able to pass through this acid. When now distilled water is gradually mixed with the acid, the amount of conducting material, in this case hydrogen

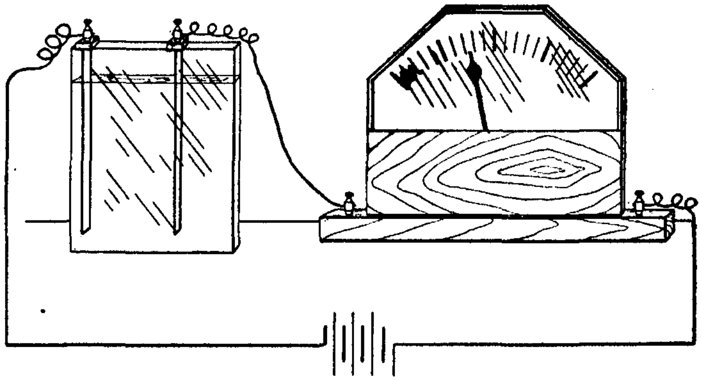


FIG. 81.

chloride, is not altered. If, therefore, its capacity for conducting were not affected by the dilution, the deflection of the needle in the amperemeter would not change. The wider dissemination of the hydrochloric acid, tending to diminish the specific conductivity of the solution, should be exactly compensated by the greater area of the electrodes coming into service. What is actually observed, however, is a very marked improvement in the conducting power of the solution.* At first the reading of the amperemeter increases very rapidly.

* The interpretation of the experiment becomes easier if the trough is first nearly filled with distilled water and the absence of deflection noted. Then a layer of concentrated hydrochloric acid is introduced below the water, by means of a long-stemmed dropping funnel, and the deflection is read. Finally, the layers are destroyed by stirring, and a great increase in the reading of the amperemeter observed. Here all the hydrogen chloride and water are between the electrodes at the time of the second reading, and the greater value of the third reading cannot be attributed to the use of a larger area of the poles, but solely to the redistribution of the acid throughout a greater volume.

Later, the effect of additional dilution becomes less marked, until finally it becomes very slight indeed.

When a saturated solution of cupric chloride is substituted, dilution is accompanied by a similar improvement in conductivity. Here we notice, besides, that the yellowish-green liquid with which we start changes to a pale blue, as the molecules of cupric chloride are dissociated and the color of the solution becomes more exclusively that of the copper ions. When the solution has become perfectly blue, further dilution is seen to affect the conductivity but slightly.

The approach to a maximum of conductivity reached in these two cases indicates that practically the whole of the material has assumed the ionic form. Theoretically the absolute maximum would be reached at infinite dilution. The conductivity of the same amount of substance in more limited dilution is that of the proportion of ions corresponding to this dilution, since the complete molecules, still present, are without influence on conductivity. Thus the ratio of the conductivity at a given dilution to the maximum conductivity is equal to the proportion of the whole material ionized at the given dilution. From a series of measurements for a fixed amount of a substance at different dilutions, after the results have been plotted, we can usually (see, however, below) ascertain the limiting, maximum conductivity by graphic extrapolation. If λ_v is the conductivity of an equivalent of the substance dissolved in v liters of water, and λ_∞ the conductivity of the same amount at infinite dilution, then λ_v/λ_∞ is the proportion of molecules completely ionized in the former solution. λ_v is called the **equivalent conductivity** at the dilution v.

The following numbers show the equivalent conductivities at 18° of solutions of four different substances, expressed in the units always employed for the purpose (which are reciprocal ohms). The symbols $\lambda_{0.1}$, meaning 1 equivalent in 0.1 l.; λ_1, meaning 1 equivalent in 1 l.; and so forth, denote the concentrations.

	$\lambda_{0.1}$	λ_1	λ_{10}	λ_{100}	λ_∞ (Calc.)
Hydrochloric acid	64.4	301.0	351.0	370.0	384
Sodium chloride	. . .	74.4	92.5	103.0	110
Sodium acetate	. . .	41.2	61.1	70.2	78
Acetic acid	0.05	1.32	4.6	14.3	(352)

It will be seen from inspection of these figures that the conductivity does not improve much in the case of the first three substances

when a solution containing one equivalent in 10 l. is diluted ten times, and that further dilutions, no matter how extensive, produce a still smaller effect. On the other hand, acetic acid conducts very badly in concentrated solution, and, while the conductivity improves with dilution, it is not possible experimentally to observe any approach to the maximum conductivity. The conductivity, in cases like this, is still far removed from the maximum at dilutions at which, with other substances, the maximum is nearly attained.

In cases like that of acetic acid, the conductivity at infinite dilution cannot be estimated by extrapolation. But fortunately another method is available. The values 384, 110, and 78 for λ_∞ in the cases of the first three substances can be reached by extrapolation, and represent the conducting powers of equal numbers of ions, for there are equal numbers of equivalents present and no molecules remain un-ionized. These values are unequal solely because of the differing speeds of the ions concerned. Each of them derives its value from numbers representing the relative speeds of the two ions present, and must be the sum of these two numbers. If, therefore, we measure the relative speeds of the two ions (p. 315), we can divide the value of λ_∞ in this proportion and learn the part which each ion contributes to the total. Dividing 384 in this way we get the speed of $H^{\cdot} = 318$ and of $Cl' = 65.9$ already given (p. 314). Dividing λ_∞ for sodium acetate (78), similarly, we get the speeds $Na^{\cdot} = 44.4$ and $C_2H_3O_2' = 33.7$. The speeds of Cl' and $Na^{\cdot}$ together (110.3) must then equal λ_∞ for NaCl, and, as we see, they do. Similarly, the speeds of $H^{\cdot}$ and $C_2H_3O_2'$ together (351.7) must equal λ_∞ for $HC_2H_3O_2'$, although we cannot observe the latter directly. This method can be applied to all of the less highly ionized acids and bases, for their sodium and potassium salts belong invariably to the class of substances which are most ionized, and for which, therefore, λ_∞ can be determined accurately by extrapolation.

Degrees of Ionization of Common Substances. — The rule, degree of ionization $= \lambda_v / \lambda_\infty$ (p. 328), enables us to calculate the value for any dilution, when the necessary data are given. We need only the values of the conductivity (λ_v) for different dilutions (p. 328) and those of the relative speeds of each kind of ions expressed in the same units. The latter, when added, give λ_∞.

Thus, hydrogen chloride in a solution containing 1 equivalent in 0.1 l. (365 g. per liter), which would be a rather concentrated hydrochloric acid, shows the degree of ionization $\frac{64.4}{384}$, or 0.168 (= 16.8 per

cent). Normal hydrochloric acid is ionized to the extent of $\frac{301}{384}$, or 0.784; normal sodium chloride, $\frac{74.4}{110}$, or 0.676; normal acetic acid, $\frac{1.32}{352}$, 0.004 (= 0.4 per cent).

Misapprehension easily arises in regard to the inferences that may be drawn from a conductivity value. A single such value, say that for salt at 10 l. dilution (92.5), gives no information about the extent of ionization. We must have the value at infinite dilution as well, that is, we must have the other term of the ratio corresponding to complete ionization, before the proportion of the molecules ionized at the 10 l. dilution can be known. Further, we must have the values of both for the same salt, at the same temperature and in the same solvent, for the values at all dilutions change markedly when any one of these conditions is altered. Thus the conductivity of normal sodium chloride solution at 50° is 120, and is therefore actually greater than that at 18° when the dilution is infinite. But at 50° the conductivity at infinite dilution is 185, so that at this temperature the degree of ionization is $\frac{120}{185}$ or 0.65, about the same as at 18°. On the other hand, when a little alcohol is added to the aqueous solution, the conductivities all diminish. But that at infinite dilution diminishes also, so that the proportion of the material ionized does not seem to be greatly affected. The chief effect of raising the temperature is simply to diminish the friction opposing the motion of the ions and, therefore, to increase the conductivity. The change is about 2 per cent for each degree. Addition of alcohol, on the other hand, increases the friction and diminishes the conductivity. There is, however, a real, though usually smaller, change in the degree of ionization with change in temperature. When the temperature is raised, the fraction ionized increases or diminishes according as the heat of ionization is negative or positive (*cf.* p. 260), and conversely when the temperature is lowered.

The following tables include the common reagents and give the proportions of ionized molecules (total molecules = 1). Except where otherwise specified, the data are for *normal solutions at 18°*. In the case of acids containing more than one displaceable hydrogen unit, the kind of ionization on which the figure is based is indicated by a period. Thus $H.HCO_3$ means that the whole of the ionization is assumed to be into $H^{\cdot}$ and HCO_3'.

FRACTION IONIZED.

ACIDS.

Nitric acid	0.820	Carbonic acid, $H.HCO_3$ (N/10)	0.0017
Nitric acid (conc., 62%)	0.096	Carbonic acid, $H.HCO_3$ (N/25)	0.0021
Hydrochloric acid	0.784	Hydrogen sulphide, $H.HS$ (N/10)	0.0007
Hydrochloric acid (conc., 35%)	0.136	Boric acid, $H.H_2BO_3$ (N/10)	0.0001
Sulphuric acid, $H.HSO_4$	0.510	Hydrocyanic acid (N/10)	0.0001
Sulphuric acid (conc., 95%)	0.007	Permanganic acid (N/2, 25°)	0.933
Hydrofluoric acid	0.070	Hydriodic acid (N/2, 25°)	0.901
Oxalic acid, $H.HC_2O_4$ (N/10, 25°)	0.500	Hydrobromic acid (N/2, 25°)	0.899
Tartaric acid, H.HT (N/10, 25°)	0.082	Perchloric acid (N/2, 25°)	0.880
Acetic acid	0.004	Chloric acid (N/2, 25°)	0.878
Acetic acid (N/10)	0.013	Hydrochloric acid (N/2, 25°)	0.876
		Phosphoric acid, $H.H_2PO_4$ (N/2, 25°)	0.170

BASES.

Potassium hydroxide	0.77
Sodium hydroxide	0.73
Barium hydroxide	0.69
Lithium hydroxide	0.63
Ammonium hydroxide	0.004
Tetramethylammonium hydroxide (N/16, 25°)	0.96
Strontium hydroxide (N/64, 25°)	0.93
Barium hydroxide (N/64, 25°)	0.92
Calcium hydroxide (N/64, 25°)	0.90
Silver hydroxide (N/1783, 25°)	0.39

SALTS.

Sodium phosphate, $Na_2.HPO_4$ (N/32)	0.83
Cupric nitrate (N/16)	0.80
Potassium chlorate (N/2)	0.79
Sodium tartrate (N/32, 25°)	(0.78)
Potassium chloride	0.75
Ammonium chloride	0.74
Sodium chloride	0.676
Sodium chloride (N/2)	0.734
Sodium chloride (N/10)	0.839
Potassium nitrate	0.64
Potassium acetate	0.64
Calcium sulphate (N/100)	0.63
Silver nitrate	0.58
Potassium sulphate	0.53
Sodium acetate	0.53
Sodium bicarbonate, $Na.HCO_3$	(0.52)
Potassium carbonate	(0.49)
Sodium sulphate	0.445
Zinc sulphate	0.24
Zinc chloride	0.48
Cupric sulphate	0.22
Mercuric chloride	($<$0.01)
Mercuric cyanide	Minute

Degree of Ionization of Water.—If we consider a liter of water as a normal solution in which 18 g. (one mole) represents the solute and the rest stands for the solvent, the conductivity for complete ionization into $H^{\bullet}$ and OH' would be $318 + 174 = 492$. The actual ionization is one ten-millionth part of this. In other words, there is only one ten-millionth of 1 g. of hydrion and the same fraction of 17 g. of hydroxidion in a liter of water. A column of water 1 cm. long conducts less well than a column of mercury of equal cross-section and over 660,000 miles in length.

General Remarks on these Values.—It will be seen from inspection of the above numbers for acids that the proportion of the molecules ionized in solutions of equivalent concentration varies enormously. Roughly, the acids might be divided into four groups: those in which the ionization exceeds 70 per cent in normal solutions; those in which it lies between 70 and 10 per cent; those in which it lies between 10 and 1 per cent; and those in which it is smaller than 1 per cent. To the first class belong the acids which we generally recognize as the most active in all their chemical relations, namely, nitric acid, the halogen hydrides, and one or two others. To the second class belong sulphuric acid and phosphoric acid, and they are less active. Amongst the acids whose ionization lies between one and ten per cent are such as hydrofluoric acid and acetic acid, and

chemically they are weak. Carbonic acid and boric acid are of the fourth class, and are feeble acids.

The bases, although less numerous, show that a similar division might be made, although in the above list only two classes are represented, — the strong bases, beginning with potassium hydroxide, and the feeble bases, represented by ammonium hydroxide.

The salts show a much greater uniformity; and, if the list had been extended so as to include the hundreds of common salts in constant use, the vast majority would have been found to show degrees of ionization lying between 50 and 80 per cent. Only a few fall below these limits. The salts of mercury are almost the only ones which would belong to the class of least ionized substances. Salts, like zinc sulphate and cupric sulphate, in which both ions are multivalent, are always much less highly ionized than are salts (*e.g.* $ZnCl_2$) made up of either of the same ions along with a univalent ion. Salts, however, are almost never restricted in their degree of ionization, to an extent sufficient to produce any noticeable effect on their chemical properties (see, however, Cadmium iodide and Mercuric cyanide).

The relation between degree of ionization and prominence of acid or basic chemical properties will be developed in the next chapter.

Comparison with the Results Obtained by Other Methods. — The value for the degree of ionization as measured by the conductivity method is coincident with that found for the same solution by a study of the abnormalities in freezing- and boiling-points and in osmotic pressure (Chap. xvii). The electrical method gives accurate results more easily than do the others, however, and is therefore the one most frequently used. It was Svante Arrhenius, a Swedish chemist, who, in 1887, first noted the coincidence in the values and devised the ionic hypothesis to account for it. From the appearance of his remarkable memoir we date the great development which the study of solutions * has undergone in recent years.

Exercises. — 1. Name (p. 322) the ionic materials furnished by the dissociation of potassium bromate, silver bromide, sodium periodate ($NaIO_4$), permanganic acid.

2. Give lists of other anions and cations which have been encountered.

* The *Scientific Memoirs, No. IV.* (American Book Company), is a reprint of the fundamental papers by Raoult, van 't Hoff, and Arrhenius.

3. How many coulombs are carried by and will deposit: 20 g. of silver, 15 g. of antimony, 30 g. of chlorine, 60 g. phosphanion (PO_4)?

4. What current strength (in amperes) is required to deposit: 20 g. of silver in an hour, 100 g. of iodine in 5 minutes, 60 g. of antimony in 3 hours?

5. What is the percentage of molecules ionized in: deci-normal (N/10) sodium chloride, centi-normal (N/100) acetic acid, centi-normal hydrochloric acid (p. 328)?

6. Give an experimental definition of the term ion. That in the text (p. 321) is in terms of the hypothesis.

CHAPTER XX

THE CHEMICAL BEHAVIOR OF IONIC SUBSTANCES

BEFORE considering the typical interactions of ionogens in solution, we must have a clear conception of the peculiarities of these bodies which are likely to affect their behavior. The facts on which such a conception must be based have been given in preceding chapters, and all that is now necessary is to collect and apply these facts. On account of the coherence which they give to the subject, the figures of speech of the ionic hypothesis will be largely employed. The reader will, therefore, do well to exercise especial care to distinguish fact from fiction.

In this discussion it must be made clear that aqueous solutions of ionogens are **mixtures** containing several solutes. It must also be shown that each kind of ions is a **distinct substance** with individual physical and chemical properties. Next, salts being used for illustration, the **commonest kind of interaction, double decomposition** between ionogens, will be discussed. In this connection **precipitation** brings up the peculiar state of equilibrium between the undissolved **solute** and the **complex of molecules and ions in solution**. Application of the same principle to special cases, such as those of **acids** and **bases**, then follows.

The discussion of systems in equilibrium in the present chapter will be purely qualitative. The quantitative consideration of ionic equilibria (*cf.* p. 297) is postponed until the study of the metals and their compounds is taken up (see Chap. xxxiv).

Solutions of Ionogens are Mixtures. — We are accustomed to regard a bottle of sodium chloride solution as containing but one thing, aside from the water. We must now think of it as containing **at least three** dissolved substances, any one of which might be alone responsible for some property of the solution. The same idea must accompany our use of every solution of an ionogen. Thus, in ordinary experiments, in which solutions of concentration not far from normal are commonly used, we have something like the following proportions (p. 330) of the three main components in six typical cases:

$(32\%) NaCl \rightleftarrows Na^{\cdot} + Cl'$ (68%), $(78\%) CuSO_4 \rightleftarrows Cu^{\cdot\cdot} + SO_4''$ (22%),
$(22\%) HCl \rightleftarrows H^{\cdot} + Cl'$ (78%), $(99.6\%) HC_2H_3O_2 \rightleftarrows H^{\cdot} + C_2H_3O_2'$ (0.4%),
$(23\%) KOH \rightleftarrows K^{\cdot} + OH'$ (77%), $(99.6\%) NH_4OH \rightleftarrows NH_4^{\cdot} + OH'$ (0.4%).

In solutions made from salts, the greater part, and by far the most active part, of the contents is almost always ionic. Cupric sulphate, being a salt both of whose ions are bivalent (p. 332), practically illustrates the lower limit as regards quantity of ions, for only a few salts of mercury and cadmium fall far below it. The acids and bases have a wider range, and a larger proportion of them are like acetic acid and ammonium hydroxide respectively. Still, even when small in amount, the ions of acids and bases are almost always much more active than the molecules.

The presence of still other components in solutions of salts, arising from interaction with the water, will be noted later.

While most of these facts are ascertained by more or less remote inference from physical and chemical properties of the solutions, some of them are evident to the eye in certain cases. Thus the progress of the ionization of a salt may be seen if one of the ions is different in color from the molecules. Cupric bromide in the solid form is a jet black, shining, crystalline substance. When treated with a small amount of water it forms a solution which is of a deep reddish-brown tint, giving no hint of resemblance to a solution of any cupric salt. This doubtless represents the color of the molecules. When more water is added, the deep brown gives place gradually to green, and finally to blue. The latter is the color of the cuprion ($Cu^{\cdot\cdot}$), and is familiar in all solutions of cupric salts. The colorless nature of solutions of potassium and sodium bromides shows that bromidion (Br') is without color. Hence, in the present instance it is invisible. We are thus watching the progress of the action:

$$CuBr_2 \rightleftarrows Cu^{\cdot\cdot} + 2Br'.$$

If 1 g. of the solid is taken, it dissolves in about its own weight of water, and independent measurement shows that there is relatively little ionization. Hence the solution is deep brown. When 10 c.c. of water has been added, 70 per cent of the salt is ionized, and the solution is green. With 40 c.c. of water, only 19 per cent remains in molecular form, and the blue color of the cuprion entirely overbears the tint of the molecules. If, at the green stage, we dissolve solid potassium bromide in the liquid, the high concentration of bromidion

which results causes an extensive reversal of the dissociation (*cf.* p. 250), and the molecules, with their brown color, become prominent again. Sufficient final dilution with water, however, reduces the concentrations of all the ions once more, the molecules dissociate, and the brown color is displaced by the blue for the second time.

Each Kind of Ion in a Mixture Acts Independently. — Numberless facts show that each kind of ion, for example cuprion, has an individual set of physical and chemical properties and behaves in many ways as if alone present in the solution. We shall meet with much evidence of this in the sequel. Some facts tending to prove it, that have already been given, may be recalled (*cf.* p. 295).

If, in comparing the migration speeds of any element, say copper, in different salts (p. 314), they were the motions of substances like $Cu(NO_3)_2$, $CuBr_2$, $CuSO_4$, that we were comparing, all analogy teaches us that the speeds with which they would move should vary widely. That the blue color drifts always at the same pace shows that it is the same substance, namely, cuprion ($Cu^{\cdot\cdot}$), that we are observing.

If, in solutions of the different permanganates, $KMnO_4$, $NaMnO_4$, $Ba(MnO_4)_2$, and so forth, the dissolved bodies were different in each case, we should confidently expect the purple colors of the solutions to differ markedly in shade. But, for dilute solutions of equivalent concentrations, when strict examination is made, the tints are found to be absolutely identical. We are therefore simply comparing different mixtures all containing the same proportion of the same free, colored body, MnO_4'.

In phosphorus pentachloride vapor (p. 255), the fully liberated trichloride and chlorine are prominent components. Diminishing the volume of a fixed amount of this mixture, by compression, throws more chlorine into combination and the total absorption (from which the greenish-yellow color is derived) becomes less, the compounds of phosphorus being both colorless. Increasing the volume, on the other hand, promotes the dissociation and increases the total absorption. The system of ions and molecules in equilibrium in a solution of cupric bromide, or any other ionogen, behaves in exactly the same way. The components possess and exhibit individual properties, much like the components of a gaseous mixture (p. 155), both in this and in other respects.

All solutions of acids are sour in taste, irrespective of the nature of the negative ion, while salts containing the same negative radical

are not sour at all. Hence in solutions of acids we are tasting the same free substance, hydrion ($H^{\cdot}$). Similarly, in solutions of all alkalies, we note the soapy taste of hydroxidion (OH').

These illustrations concern physical properties. In the next section we shall learn that an ionic material, such as bromidion or cuprion, has specific *chemical* properties irrespective of the nature of its concomitants.

Salts, Ionic Double Decomposition, Precipitation.

Salts. — We have already seen that salts differ much in solubility in water, that some combine with water to form solid hydrates (p. 120), that they interact with acids, bases, and other salts by exchange of radicals, reversibly (p. 281), and that they are all ionogens.

Both the positive and negative ions of salts may be simple or composite, Na.Cl, $Na.NO_3$, $NH_4.Cl$, $NH_4.NO_3$. The elements which can form a simple positive ion are known in chemistry as **metals** (p. 119, and see Chaps. xxiii and xxxii). Non-metals, like nitrogen, may be present in a positive ion, as in $NH_4^{\cdot}$, but never exclusively. In other words, we know no such substances as nitrogen sulphate, or carbon nitrate. Metals, on the other hand, are frequently found in the negative ion, but never constitute it exclusively. They are then usually associated with oxygen, as in MnO_4', and Cr_2O_7''. Some ionic materials are colored, $Cu^{\cdot\cdot}$ blue, $Cr^{\cdot\cdot\cdot}$ reddish violet, $Co^{\cdot\cdot}$ pink, MnO_4' purple, Cr_2O_7'' orange, but most of them are colorless, $K^{\cdot}$, $Na^{\cdot}$, $Zn^{\cdot\cdot}$, Cl′, I′, NO_3'. The ions of salts do not affect litmus. They vary in taste, some being salt, some astringent, some bitter. In dilute solutions they are almost always numerous in comparison with the surviving molecules. They carry electricity, but relatively less well than do hydrion and hydroxidion, on account of their slower migration. All the known ionic materials are found in solutions of salts. The only ions which are not characteristic of salts, although sometimes occurring in their solutions (see Mixed ionogens), are hydrion $H^{\cdot}$, and hydroxidion, OH′.

Double Decomposition of Salts in Solution. — When we mix sodium chloride (NaCl) and silver nitrate ($AgNO_3$), both in solution in water (H_2O), there would seem to be many different possibilities of union amongst the six elements represented in the mixture. But only one sort of change occurs, and it takes place almost completely:

$$AgNO_3 + NaCl \rightleftarrows AgCl\downarrow + NaNO_3. \qquad (1)$$

So in general, we find that a single crosswise union of ions with opposite electrical charges is by far the commonest kind of interaction between ionogens. There are indeed four other kinds of ionic chemical change, as will be seen in the sequel, but for the present we shall discuss only the cases of double decomposition.

When solutions of two ionized substances are mixed, the first reflection which occurs to us is that each of these has been diluted by the water in which the other was dissolved, so that the first effect will be to increase the degree of ionization of both to a certain extent. The next consideration is, however, that we have produced a mixture of four ions, which must have at least some tendency to unite crosswise. Thus potassium chloride and sodium nitrate in dilute solution are very greatly ionized before mixing. The reversible actions, represented by the horizontal pair of the following equations, have taken place extensively. But, by mixing the liquids, we have brought into presence of one another two new pairs of positive and negative ions. Hence, two other reversible actions, the vertical ones,

$$\begin{array}{rcll} KCl & \leftrightarrows & K^{\cdot} & + \ Cl' \\ NaNO_3 & \leftrightarrows & NO_3' & + \ Na^{\cdot} \\ & & \updownarrows & \quad \updownarrows \\ & & KNO_3 & \quad NaCl \end{array}$$

will be set up and will proceed until a fresh equilibrium of all the ions with all four kinds of molecules has been reached. Examination of the solutions of these four salts, separately, shows that they are in an equal degree extensively ionized in dilute solutions, so that in this particular case the whole quantity of molecules of all kinds will not be very great. That this inference is correct is shown by much independent evidence, of which two samples may be given.

The change of ionic materials into molecular and *vice versa* is always accompanied by absorption or liberation of heat (p. 330). Now it was for long a matter of surprise that when dilute solutions of salts, as distinct from pairs which included acids or bases (*q.v.*), were mixed, no heat-change was observable. This fact was called the thermoneutrality of salts, but the reason for it was unknown. Since salts are *all* highly ionized, the reason is now apparent. Similarly, no changes in color or volume accompany the mixing of dilute solutions of salts.

Again, any of the means which may be used for measuring the number of molecules, including ions, in a solution, may be applied to learning whether any appreciable proportion of the latter has disap-

peared. Osmotic pressure, freezing-point, boiling-point, and conductivity are all applicable. The last lends itself best to the purpose of demonstration. The cell and amperemeter described in the last chapter (Fig. 81) may be employed. We place in the cell a one-fourth normal (N/4) solution of potassium chloride and introduce an equal volume of N/4 sodium nitrate, in such a way that it forms a separate layer beneath the other solution. We read the amperemeter, mix the liquids by stirring, so as to permit chemical interaction to take place, and then note the conductivity once more. There is no observable change in the conducting power, and, therefore, no appreciable change in the condition of the ionic substances has taken place.

We shall have occasion in a later paragraph to show that, where the ions unite crosswise to an appreciable extent, an experiment of this kind shows a marked diminution in the conductivity, corresponding to the amount of combination that has occurred. In such cases, also, heat is either liberated or absorbed.

It thus appears that when dilute solutions of *salts* are mixed, and there is *no visible evidence of chemical change*, the little that has taken place may be neglected. Practically, mixing of this kind is a physical operation. Of course, in the event of one product being precipitated, a diminution in the conductivity, corresponding to the amount of ionic material removed, will be observed.

In view of the above explanation, the old question of whether such a solution contains the first pair of salts, or the second pair, represented in the double decomposition, $KCl + NaNO_3 \rightleftarrows KNO_3 + NaCl$, loses its whole point. The solution contains neither the initial molecular substances nor the molecular products, in appreciable amount.

Solution and Precipitation of Salts. — In a body which is dissolving or being precipitated, we are observing the progress of a reversible physical operation (p. 153):

$$\text{Molecules (undiss'd)} \rightleftarrows \text{molecules (diss'd)}.$$

If the molecules are sparingly soluble, the forward action is feeble, while the backward one, when we start with the same material in solution, makes great progress. Conversely, when the substance is a soluble one, the forward action comes to a standstill (or the reverse action occurs) only when the concentration of dissolved molecules has become very large.

Now it will be noted that this mechanical adjustment concerns only the *molecules*, and that the ions, if there are any, are involved

only indirectly. The ions are in equilibrium with the *dissolved* molecules:

$$AB \text{ (undiss'd)} \rightleftarrows AB \text{ (diss'd)} \rightleftarrows A^{\cdot} + B'.$$

Hence, when a substance dissolves, it does so in molecular form, and ions are subsequently generated from some of these molecules until equilibrium is reached. Conversely, when molecules come out of solution, as the result of cooling, for example, the diminished concentration of the central term of the chain enables more ions progressively to unite until the whole system has adjusted itself to the new conditions.

Now this has an important bearing on the result of mixing dilute solutions of two soluble salts. We have seen that the concentration of the molecules of the new pair of salts is never large. Yet it may easily be in excess of the amount which the water can hold in solution, if one of the salts is of the relatively insoluble class. This occurs, for example, when a chloride is mixed with a salt of silver. The system of equilibria, leaving out that of $Na^{\cdot}$ and NO_3', and rearranging (*cf.* p. 338), so as to save space, appears as follows:

$$\left.\begin{array}{l} NaCl \rightleftarrows Na^{\cdot} + Cl' \\ AgNO_3 \rightleftarrows NO'_3 + Ag^{\cdot} \end{array}\right\} \rightleftarrows AgCl \text{ (diss'd)} \rightleftarrows AgCl \text{ (solid)}. \qquad (2)$$

The concentration of dissolved silver chloride which the solid can maintain in solution being very minute, most of this salt is at once precipitated. The ions continue to unite because the requisite concentration of molecules, whose dissociation should bring their union to a standstill, has not been kept up. The new molecules are in turn precipitated. The system reaches a stable condition only when the concentration of chloridion (Cl') and argention ($Ag^{\cdot}$) has fallen to that which can be maintained by the mere trace of molecules which the insolubility of the substance permits to remain in solution. When the system of equilibria is examined, we see at once what the result must be. The removal of chloridion and argention enables the remaining molecules of sodium chloride and silver nitrate to become completely ionized. Thus the concentration of NaCl and $AgNO_3$, of $Ag^{\cdot}$ and Cl' and of the dissolved AgCl, all become practically zero. The system finally contains only molecular, solid silver chloride and the three substances, $Na^{\cdot} + NO_3' \rightleftarrows NaNO_3$, in equilibrium, of which by far the greater part is the ionic. There is therefore in the action much detail which the first equation (p. 337) did not show.

The above explanation will apply to any case of precipitation resulting from the interaction of ionogens. If the least soluble of the four salts is more soluble than silver chloride, more concentrated solutions are required to secure precipitation. The interaction of hydrogen chloride and sodium hydrogen sulphate (p. 179) is of this nature:

$$\left.\begin{array}{l} HCl \leftrightarrows H^{\cdot} \quad + Cl' \\ NaHSO_4 \leftrightarrows HSO_4' + Na^{\cdot} \end{array}\right\} \leftrightarrows NaCl \text{ (diss'd)} \rightleftarrows NaCl \text{ (solid)}.$$

It should be noted that, strictly speaking, the only interaction taking place when the solutions are mixed is the production of the *insoluble* body. In the case of silver chloride, (1) and (2), the largest part of the chemical action may be formulated thus:

$$Ag^{\cdot} + Cl' \leftrightarrows AgCl. \qquad (3)$$

The chief change that has as yet befallen the ions of sodium nitrate is that they have been transferred from two separate vessels into one. Potentially the salt has been formed. But the actual union of its ions to give the second product in the molecular condition:

$$Na^{\cdot} + NO_3' \rightarrow NaNO_3, \qquad (4)$$

comes about only when, at some subsequent time, if at all, the water is evaporated away.

Individual, Specific Chemical Properties of Each Ionic Material. — We wrote the equation for the formation of silver chloride ($Ag^{\cdot} + Cl' \rightarrow AgCl$) as if argention and chloridion were the only substances concerned in the action. Further study shows this to be justifiable. Thus, hydrochloric acid, cupric chloride, and dozens of other chlorides may be used instead of sodium chloride and give silver chloride just as readily. The natrion had nothing to do with the result. Of course we cannot get a solution containing chloridion alone. Like a vessel in which to make the experiment, some positive ion is required. But, like the rest of the apparatus, this ion may be varied indefinitely, is not altered in the course of the change, and may therefore be dispensed with in the equation. The nitranion (NO_3') which accompanied the argention is similarly a part of the apparatus, for silver sulphate solution works just as well as silver nitrate.

That chloridion is a substance with specific chemical properties, is easily demonstrated. It forms silver chloride whenever it encounters argention. Other substances, even when they contain chlorine, lack

this property. Chloroform ($CHCl_3$) and chlorobenzene (C_6H_5Cl), in a solvent in which ionogens are dissociated, do not interact when silver nitrate is added. They give no chloridion, and, in fact, remain un-ionized. Potassium chlorate ($KClO_3$) and perchlorate ($KClO_4$) and chloracetic acid ($HC_2H_2ClO_2$), with argention, fail likewise to give silver chloride. They are ionized, but chloridion is not one of the ions of any of them. The ions ClO_3', ClO_4', and $C_2H_2ClO_2'$, have properties of their own, and their compounds with argention are soluble.

Other chemical properties of chloridion are: That it unites also with plumbion ($Pb^{\cdot\cdot}$) and monomercurion ($Hg^{\cdot}$), forming insoluble chlorides (p. 185). It is discharged and liberated as free chlorine by fluorine (p. 241):

$$2H^{\cdot} + 2Cl' + F_2 \rightarrow 2H^{\cdot} + Cl_2 + 2F'.$$

Since the hydrion is not affected and many chlorides behave in a similar manner, the positive ion may be omitted:

$$2Cl' + F_2 \rightarrow Cl_2 + 2F'.$$

Finally, chloridion has relatively little tendency to unite with other ions, or, in other words, the compounds of chloridion with most other ions are highly ionized. Thus it combines with hydrion to the extent of only 22 per cent (p. 330) in normal solution. In this respect it differs markedly from free chlorine, just as hydrion differs from hydrogen. The free elements unite with vigor and completely. Hydrogen chloride is easy to dissociate into ions, but difficult to dissociate into its constituent elements. Nothing could show more strikingly than this that the ionic materials have chemical properties of their own.

Similarly, barium salts and ordinary sulphates give, when mixed, a precipitate of barium sulphate. Here we encounter a property of barion ($Ba^{\cdot\cdot}$) and sulphanion (SO_4''). But potassium ethyl sulphate ($KC_2H_5SO_4$), in spite of its name, will not give this reaction with a barium salt. Here electrolysis shows that sulphanion is absent and that the negative ion is $C_2H_5SO_4'$.

In the same way every other ionic material may be shown to be a substance with an individual set of physical (p. 336) and chemical properties. Each salt, when dissolved, gives two kinds (see, however, below) of ionic materials. The solution is simply a mixture, and each physical component forthwith behaves towards ions capable of uniting

with it, as if it were alone. The other materials, ionic and molecular, which are present, may remain essentially unaffected throughout the change.

Application in Chemical Analysis. — Since the larger number of ordinary chemical substances are ionogens, and the most rapid and simplest chemical changes take place when they are in solution, the various reactions of their solutions are employed as tests for the substances in question. An advantage of the use of the solutions is that they contain a mixture of two independent materials, the anion and the cation, and when these have been identified successfully the salt from which they were formed is known. The simplicity to which chemical analysis is thus reduced may be seen when we consider that twenty-five common metals with twenty-five negative radicals might give a total of over six hundred different salts. If the distinct properties of each of these had to be considered, the identification of an unknown substance would be very difficult. In solution, however, the problem becomes much easier. Every solution made from a single salt will contain but two substances (in the main; see, however, below), and the problem reduces itself to ascertaining which two, out of a total of fifty, are present in any particular case.

As an example of the method, let us suppose that we look first for the positive ion. Most systems of analysis begin by the addition of a solution containing chloridion, generally dilute hydrochloric acid, to the liquid. If an ion is present which in combination with chloridion gives an insoluble compound, a precipitate will appear. Amongst the common positive ions but three are of this kind, namely, argention, monomercurion, and diplumbion. So that the precipitate, if it appears, is a chloride of one of these three metals, and the matter of distinguishing between the three is quickly disposed of by further examination of its properties. If no precipitate comes out, then these three metals are probably absent, and some fresh ion capable of precipitating another set of positive ions is introduced (see Chap. xxxvii). Thus by a process of elimination we quickly find out whether any metal ion is present, and, if so, precisely which one it is.

The language of analysis is frequently somewhat loose. Thus we speak of the addition of a silver salt to a solution as being a "test for chlorine." As a matter of fact, it is not a test for chlorine. It is not intended as a test for free chlorine, nor will it show the presence of chlorine in many states of combination. It is simply a test for ionic chlorine (Cl'), and cannot give us information in regard to the presence or absence of any other form of the element. So the wet-way tests for "copper," "silver," etc., so called, are tests for the ionic forms of these elements, and not for the presence of the element in every form. Even the two kinds of copper and mercury ions, $Cu^{\cdot\cdot}$, $Cu^{\cdot}$, $Hg^{\cdot\cdot}$, $Hg^{\cdot}$, must be classed as distinct substances. Thus, the last is precipitated by chloridion while the second last is not, mercuric chloride ($HgCl_2$) being soluble.

Hydrolysis of Salts. — The natural ionization of water is very slight, but there are cases in which its effects become noticeable, and the interaction of its ions with those of dissolved salts cannot be neglected. For example, an aqueous solution of pure cupric sulphate is always acid and therefore contains hydrion :

$$\left.\begin{array}{l} CuSO_4 \leftrightarrows SO_4'' + Cu^{\cdot\cdot} \\ 2H_2O \leftrightarrows 2H^{\cdot} + 2OH' \end{array}\right\} \leftrightarrows Cu(OH)_2 \text{ (diss'd).}$$

Cupric hydroxide, being a very feeble base, and comparable with water itself in the small extent to which the solvent is able to hold its ions apart, is formed to a small extent. The removal of some hydroxidion by this means enables more of the water to dissociate. This, in turn, furnishes the material for the production of more cupric hydroxide. The action does not proceed very far, but it makes sufficient progress to leave a perceptible excess of hydrion in the liquid and to give it, therefore, an acid reaction. The hydrion combines slightly, but only slightly, with the sulphanion, for sulphuric acid is a highly ionized acid. This part of the action has, therefore, been left out of the diagram. The ordinary equation for this change would be:

$$CuSO_4 + H_2O \leftrightarrows Cu(OH)_2 + H_2SO_4.$$

The hydrolysis is much greater with sodium sulphide (*q.v.*) and antimony trichloride (*q.v.*).

Again, soap solution is always faintly alkaline:

$$\left.\begin{array}{l} C_{15}H_{31}CO_2Na \leftrightarrows Na^{\cdot} + C_{15}H_{31}CO_2' \\ \qquad H_2O \leftrightarrows OH' + \quad H^{\cdot} \end{array}\right\} \leftrightarrows HC_{15}H_{31}\,CO_2 \text{ (diss'd).}$$

The sodium palmitate is highly ionized, but palmitic acid ($HC_{15}H_{31}CO_2$) is hardly ionized at all. The final result is the production of a recognizable amount of hydroxidion in the solution. Thus, a salt derived from an acid and a base of very different degrees of activity, whether it is the base (as $Cu(OH)_2$) or the acid (as palmitic acid or hydrogen sulphide, *q.v.*) which is the weaker member, is likely to be more or less hydrolyzed by water. In the former case the solution is acid, in the latter basic in reaction. Other things being equal, salts containing bivalent or trivalent radicals are more noticeably hydrolyzed than are those composed only of univalent radicals.

Cases of this kind being common, we are thus compelled to enlarge our list of possible components in the solutions of any salt. In addi-

tion to the molecules and ions of the salt, there are present, water and its ions, and the molecules of the base and acid formed by the union of the latter ions with the former. There are thus no less than *eight different components* in the mixture.

Acids and Bases and Their Double Decomposition with Salts.

Hydrogen Salts. — The substances of the composition HCl, H_2SO_4, and so forth, are commonly called acids, and when more convenient we shall conform to this usage. But it is only when they have been dissolved in water or some other ionizing solvent that they show the properties characteristic of acids. In fact, in terms of the ionic hypothesis, there is only one acid, hydrion ($H^{\cdot}$), although the substances which give it by dissociation are many. The parent substances are salts of hydrogen, in which the element hydrogen plays the part of a metal.

The properties of the hydrogen salts, that is, of the original ionogens, are the same as those of any other ionogens. **They are distinguished from other ionogens by the fact that their positive radical is always hydrogen and that in solution they yield hydrion.** Their negative radicals are all different, Cl, Br, I, ClO_3, ClO_4, BrO_3, NO_3, and so forth. These radicals form the negative ions in solutions of hydrogen salts. In such solutions all the properties of these ions are the same as when they are furnished by dissolving other salts containing the same radicals. **Some hydrogen salts have oxidizing powers** like hypochlorous acid (p. 269). Usually, **they exchange radicals with the other ionogens.** They often do this even when dissolved in non-dissociating solvents. They frequently do it also in the absence of a solvent, especially when heated. They differ from one another in the matter of solubility in water, some being almost insoluble. By solution in water **they give acids of very different degrees of activity** (see Activity of acids, below).

Hydrion. —Hydrion is a colorless substance which exists in water and certain other solvents only. It is always associated with an equivalent amount of some negative ion. It is sour in taste, and its presence is recognized by the fact that it turns blue litmus red and decolorizes pink phenolphthaleïn (see Indicators, below) solutions. It confers a high conducting power upon solutions in which it is contained, on account of its great speed of migration. It is univalent and combines

with negative ions, such as hydroxyl and the negative radicals of salts. It is displaced by metals like magnesium. In all these respects it differs markedly from free hydrogen gas.

The displacement of hydrogen from dilute acids (p. 95) now appears in a new light. The action will be formulated thus:

$$Zn + 2H^{\cdot} + SO_4'' \rightarrow Zn^{\cdot\cdot} + SO_4'' + H_2.$$

The sulphanion (SO_4''), although zinc sulphate is somewhat less ionized than sulphuric acid, is not much affected by the change and may be omitted:

$$Zn + 2H^{\cdot} \rightarrow Zn^{\cdot\cdot} + H_2.$$

Thus, this action, which takes place in the same fashion with most acids, is seen to be independent of the nature of the negative ion. It consists simply in the transference of the electric charges from the hydrogen to the zinc, whereby the latter becomes ionic. The discharged hydrogen is liberated as gas. When the solution is evaporated, the ionogen, in the above case zinc sulphate, is formed:

$$Zn^{\cdot\cdot} + SO_4'' \rightarrow ZnSO_4.$$

Modes of Ionization of Acids. — An acid containing but one unit of hydrogen in its molecule can give but two kinds of ions. Thus, chloric acid gives only $H^{\cdot}$ and ClO_3'. When more than one hydrogen unit is present, however, more than two kinds of ions are formed. Thus, sulphuric acid, H_2SO_4, produces, in the first place, hydrosulphanion:

$$H_2SO_4 \rightleftarrows H^{\cdot} + HSO_4'.$$

The latter is also an acid, but is considerably *less active* than sulphuric acid. Hence, the further dissociation of this ion ($HSO_4' \rightleftarrows H^{\cdot} + SO_4''$) lags considerably behind the primary dissociation. In concentrated solutions of the acid there is, therefore, much HSO_4' present. In very dilute solutions, however, SO_4'' predominates. We know that HSO_4' is a weaker acid, and is dissociated with greater difficulty by water, because acid salts (see below), like $KHSO_4$, which give this ion, are much weaker acids than are acids like HCl and $HClO_3$, with which the substance HSO_4' might fairly be compared. This behavior is not peculiar to sulphuric acid, but is shown by all acids containing more than one hydrogen unit in the molecule (*cf.* Hydrogen sulphide).

Activity of Acids. — In solutions containing equivalent quantities of hydrogen salts, and therefore equal amounts of *combined* hydrogen, in equal volumes, the concentration of hydrion present at any moment in each will be different. This concentration will be high or low according to the extent to which water is able to dissociate the molecules. Now the activity of the hydrion, that is, the speed with which it will interact, like that of any other substance, depends on its concentration (p. 250). Hence the hydrogen salts furnish, on being dissolved, acids of all degrees of activity. Thus in normal hydrochloric acid, the fraction dissociated is 0.78, and the hydrion is 0.78–normal, whereas in normal acetic acid the hydrion is only 0.004–normal (p. 330). Yet the amounts of hydrogen chloride and hydrogen acetate per liter contain equal quantities of combined hydrogen, namely, 1 g. each. Both the solutions in fact are normal in respect to combined hydrogen. But the normal acetic acid has only about one two-hundredth of the activity of normal hydrochloric acid.

That a difference in the activity of different acids does exist may be shown, roughly, by placing similar pieces of the same metal, say zinc, in equal volumes of various normal solutions of acids, such as hydrochloric, sulphuric, and acetic. The hydrogen is evolved more rapidly by the first than by the second, and very much faster by either than by the last. Naturally, the first is sooner exhausted, while the third acts in its slow way for a very long time before being all used up. In the third case few ions of hydrogen are at hand at any one moment, but more are formed continuously from the molecules, to take the place of those displaced. Thus the total amount of hydrogen obtained from each acid is finally the same. It is *the speed of evolution alone which is different* and shows the differing concentrations of the hydrion.

In cases of extremely small ionization, the presence or absence of visible action on litmus may form another means of estimating activity. Thus, litmus is *easily* turned red by a deci-normal solution of acetic acid or of any more active acid (p. 330), but hydrogen sulphide, in a solution of the same molecular concentration, contains only one-twentieth as many hydrogen ions (p. 330), and affects litmus paper but slightly. Paper dipped in Congo red exhibits differences in the activity of acids by the different depths of the tints it assumes. For example, it is much less markedly affected by acetic than by sulphuric acid of the same concentration (see Indicators, below).

Many hydrogen salts are but slightly soluble. Thus, with silicic

acid (*q.v.*), the solid can keep only a small concentration of molecules in solution: H_2SiO_3 (solid) $\leftrightarrows$ H_2SiO_3 (diss'd). So that, although some ions are doubtless present, H_2SiO_3 (diss'd) $\rightleftarrows$ $2H^{\cdot} + SiO_3''$, their concentration, being dependent on that of the molecules, is very minute indeed. Still, even in the absence of an effect upon litmus, the substance can be recognized to be an acid. Thus, by the action of sodium hydroxide, silicic acid can be made into sodium silicate, Na_2SiO_3, which is highly soluble and highly ionized. Hence, since SiO_3'' is a negative ion, we reach the conclusion indirectly that H_2SiO_3 is an acid.

Substances like ammonia NH_3, sugar, and alcohol, although they contain hydrogen, are not hydrogen salts. They are not ionogens (*cf.* p. 281), and give no hydrion. Ionizable and non-ionizable hydrogen may even be contained in the same compound. Thus, each molecule of acetic acid ($HC_2H_3O_2$) contains four hydrogen units, but gives only one hydrogen ion. The other three are part of the acetanion ($C_2H_3O_2'$). We infer this because metals can be substituted for one hydrogen unit ($NaC_2H_3O_2$), but not more.

Salts of Hydroxyl.—Substances like potassium hydroxide, ammonium hydroxide (NH_4OH), and zinc hydroxide ($Zn(OH)_2$), are commonly called bases. But it is only in their aqueous solutions that the basic properties appear. There is only one base, namely, hydroxyl (OH'), and these substances are simply the source of it. The parent substances are salts of some metal, or group playing the part of a metal (*e.g.* NH_4), in which hydroxyl is the negative radical.

The more active bases are called **alkalies**, sometimes caustic alkalies and, individually, often, caustic potash, and caustic soda. The solutions are called lyes.

The name "base" was originally applied to the non-volatile, and therefore seemingly more fundamental part of a salt that remained behind when the salt was heated. Usually the negative radical is disintegrated, as in heating calcium carbonate (*q.v.*). But, as a matter of fact, it is generally the oxide and not the hydroxide of the metal that remains. Still, the oxide, formerly named the base, often readily gives the hydroxide (*cf.* p. 119) of which the term "base" is now used, and behaves similarly to it in many interactions (*cf.* p. 186).

The **salts of hydroxyl** have the properties common to all ionogens. **They are distinguished from other ionogens** by the fact that their negative radical is always hydroxyl **and that in solution they yield hydroxidion.** Their positive radicals are all different, K, Na, NH_4, Zn, Cu, etc., and constitute the positive ions of solutions of the bases.

All the properties of these ions in such solutions are the same as when these ions are formed in solutions of salts containing the same radicals. Usually the salts of hydroxyl **undergo double decomposition with other ionogens, exchanging radicals**, even in absence of a solvent. Like hydrogen salts (p. 347) they are ionized to different degrees when in solutions of equivalent concentration, giving solutions with *different* concentrations of hydroxidion. Hence, **they give solutions of different degrees of basic activity.**

The common bases, with the exception of the hydroxides of potassium, sodium, barium, strontium, calcium, and ammonium, are but slightly soluble in water. Hence, zinc hydroxide, for example, although it dissolves sufficiently to enable chemical action to take place slowly, does not give enough hydroxidion at one time to affect litmus paper. Magnesium hydroxide and lead hydroxide turn red litmus paper blue with difficulty. Doubtless the few molecules that do dissolve are almost all ionized:

$$Mg(OH)_2 \text{ (solid)} \leftrightarrows Mg(OH)_2 \text{ (diss'd)} \leftrightarrows Mg^{\cdot\cdot} + 2OH',$$

but all the dissolved materials put together (0.01 g. per l.) will scarcely be weighable unless a considerable volume of the solution is evaporated.

Hydroxidion. — Hydroxidion is a colorless substance found only in water and certain other solvents, and is always associated with an equivalent amount of some positive ion. It possesses a soapy taste, and turns red litmus blue and colorless phenolphthalëin pink (see Indicators, below). It confers great conducting power upon solutions in which it is contained, on account of its speed of migration which is second only to that of ionic hydrogen. It is univalent and unites with positive ions.

Ionic Double Decomposition and Precipitation of Acids and Bases. — Under this head, we shall discuss only the interaction of a salt with an acid or base, reserving for a separate section, on neutralization, that of acids and bases with each other.

When a highly dissociated **acid is mixed with a salt**, a reversible action tending to form another acid and salt is set up (p. 264). Such an action is that of nitric acid on a hypochlorite (p. 267) in dilute solution:

$$HNO_3 + KOCl \leftrightarrows KNO_3 + HOCl,$$

giving potassium nitrate and hypochlorous acid. In such a case, if the products are both as highly ionized as the initial substances, the result is similar to that of the interaction between potassium chloride and sodium nitrate (p. 338). No decisive change takes place.

With hypochlorous acid, however, which is very slightly ionized, the result is different:

$$\left.\begin{array}{l} HNO_3 \leftrightarrows NO_3' + H^{\cdot} \\ KOCl \leftrightarrows K^{\cdot} + OCl' \end{array}\right\} \leftrightarrows HOCl \text{ (diss'd)}.$$

This acid is promptly formed from its ions, and the final mixture contains, mainly, $K^{\cdot}$, NO_3' and molecular HOCl. Yet, since the substance is soluble, no outward evidence that the action differs from that of potassium chloride and sodium nitrate is visible. The conductivity of the mixture (p. 339), however, is found to have been greatly reduced by the removal of half the ions, including the most rapidly migrating of the four, hydrion (p. 314).

When the molecules of the resulting acid are insoluble, then it may be precipitated (*cf.* silicic acid), after the manner of silver chloride (p. 340), or may escape if a gas (*cf.* hydrogen sulphide), irrespective of its degree of ionization.

In the same way, when a **salt and a base** are brought together, a base and a salt are produced. All that has been said in the preceding paragraph applies to this case also. Thus ammonium hydroxide (*q.v.*), which is a feebly ionized base (p. 331), is formed on this plan, by mixing solutions of an ammonium salt and a strong base:

$$NH_4Cl + NaOH \leftrightarrows NaCl + NH_4OH.$$

When the resulting base is insoluble, like zinc hydroxide, it is precipitated, and the action becomes nearly complete on this account and irrespective of the degree of ionization.

Ionic Double Decomposition and Activity. — It is quite clear that the complete formation of acids, bases, and salts by precipitation is purely a result of mechanical details concerning solubility, and shows nothing about the degree of affinity between the constituent ions. Again, the union of ions to form feebly ionized substances only shows the tendency of the *ionic* materials to unite and may be complete where the free elements have little mutual activity, and *vice versa*. Thus, hydrion and hypochlorosion (ClO′) unite almost completely, while hydrion and chloridion hardly unite at all. Yet hypo-

chlorous acid is very unstable, while hydrogen chloride is just the reverse. Ionic double decompositions, consequently, give no clue to the activities of the free materials.

Neutralization.

Neutralization. — When 80 per cent sulphuric acid is poured upon solid potassium hydroxide, much heat is developed and clouds of steam arise. The solid product, when freed from the rest of the water, is potassium sulphate. The proportions of the materials used and produced are shown by the equation:

$$2KOH + H_2SO_4 \leftrightarrows 2H_2O \uparrow + K_2SO_4.$$

With any other pair consisting of an acid and a base, a similar interaction occurs (*cf.* p. 266), water and a salt being produced.

A double decomposition between ionogens is always reversible (p. 281), and so we should expect that in dilute solution the interaction of an acid and a base would be incomplete. We find, however, that this particular sort of action almost always goes so near to completion that it can be employed for exact measurement of the quantity of the acid or base. This kind of action is called **neutralization**, because both acid and base are completely consumed, and hydrion and hydroxyl are alike impossible of detection in the resulting mixture. The solution is **neutral** to litmus.

Acidimetry and Alkalimetry. — If the problem is to ascertain the weight of hydrogen chloride in each liter of a specimen of hydrochloric acid, this can be done by neutralizing a measured portion of this acid with a solution of an alkali of known concentration. The volume of the latter which is required for the purpose is observed. If the alkali is sodium hydroxide, the action taking place is:

$$HCl + NaOH \rightarrow H_2O + NaCl.$$

The volume of acid is measured out into a beaker by means of a pipette (Fig. 82) of fixed capacity, which is filled by suction to the mark on the stem. Suppose the amount to be 25 c.c. The standard (*cf.* p. 236) alkali solution is placed in a burette (Fig. 83), which is filled down to the tip of the nozzle. A few drops of litmus solution are now added to the acid, and the alkali is allowed to run in slowly. After a time, the hydroxidion which this introduces will begin to pro-

duce a blue color close to where the stream enters the liquid. This is at first dissipated by stirring, and the whole remains red. Finally, however, a point is reached at which the entire solution assumes a tint intermediate between blue and red. With one drop less of the base, it is distinctly red. With one drop more, it would become distinctly blue. Litmus paper of either shade dipped in this neutral solution remains unaffected. It is needless to say that the acid might have been added to the base with the same final result.

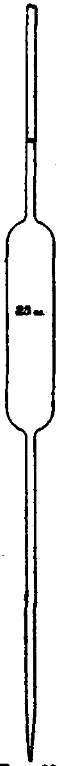


FIG. 82.

The standard solutions used in this work are usually normal, and contain one equivalent weight of the alkali or acid in one liter of the solution. For more delicate work, deci-normal solutions may be employed. The concentration of such a solution is called its **titer**, and the operation of neutralizing another solution by means of it, **titration**. The value of standard solutions lies in the fact that when once the solution has been prepared, and the exact concentration adjusted by quantitative experiments, its use does not require any weighing, and the measurements of volumes can be carried out with great rapidity. A process involving weighing need not again be undertaken until the stock of the standard solution is exhausted. The calculation of the result is also simple. One liter of normal alkali contains 17 g. of available hydroxyl, and one liter of normal acid 1 g. of available hydrogen. Equal volumes of normal solutions will therefore exactly

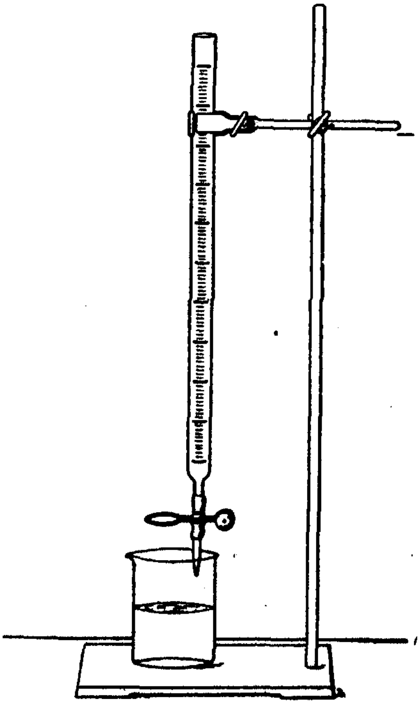


FIG. 83.

neutralize one another, 18 g. of water being formed by interaction of a liter of each. If, for the neutralization of the 25 c.c. of hydrochloric acid used above, 50 c.c. of normal alkali are required, the acid is twice-normal (2N). When 15 c.c. are required, the acid is $\frac{15}{25}$ or $\frac{3}{5}$ N. If the actual weight of hydrogen chloride in the latter case has to be calculated, we remember that there are 36.45 g. of the compound in 1 l. of a normal solution, and therefore $36.45 \times \frac{3}{5} \times \frac{25}{1000}$ g. = 5.466 g. in 25 c.c. of one which is $\frac{3}{5}$ normal.

Methods of quantitative analysis in which standard solutions (*cf.* pp. 148, 236, 307) are employed are known as **volumetric** methods, and are much used by analysts and investigators. They occupy much less time than **gravimetric** operations, in which numerous weighings have to be made, and are often just as accurate. The substances, like litmus, by whose change of color the completeness of the action is made known, are called **indicators** (see below).

Theory of Neutralization. — The neutral mixture of the acid and base gives no evidence of the presence either of the hydrogen ions or of the hydroxyl ions. The characteristic tastes, and actions upon indicators, of these two ions, and the interaction of the former of the two with metals like magnesium, are all wanting. That this is due, not simply to two opposing influences having destroyed each other's effects, but to a real disappearance of the agencies themselves, may be demonstrated by showing that the total number of ions is very much smaller in the mixture than in the two substances taken separately. The trough (Fig. 81, p. 327) is half-filled with a dilute solution (say, N/4) of some active acid, such as hydrochloric acid. An equal volume of a N/4 solution of some soluble base, such as sodium hydroxide, is then allowed to flow in, below the acid. On completing the circuit we find a considerable deflection of the amperemeter (say, 1.5 amperes). When the interaction is now brought about by stirring, a very great fall in the reading (say to 0.5 amperes) is observed.* The only plausible explanation is that, not only have many of the ions assumed a molecular form, but those which have suffered in this respect have been the most rapidly moving and best conducting ones, namely, the hydrion and hydroxidion.

* The experiment may be made more striking by adding a few drops of phenolphthaleïn solution to the acid and using a *minute* excess of the base. To prevent the appearance of a pink layer at the interface, and before the stirring, a thin layer of sodium chloride solution may be introduced below the acid, before the layer of the base is added.

The general plan of all interactions of acids and bases is as follows:

$$\begin{array}{rcl} HCl & \rightleftarrows & Cl' + H^{\cdot} \\ NaOH & \rightleftarrows & Na^{\cdot} + OH' \\ & & \ \ \downarrow\uparrow \qquad \downarrow\uparrow \\ & & NaCl \quad H_2O \end{array}$$

The ionization of the hydrochloric acid reaches 0.785 in a normal solution, and goes further when the acid is diluted with the water of another solution. That of the sodium hydroxide similarly goes beyond 0.73. Thus the initial substances are almost entirely ionic. The crosswise union, $H^{\cdot} + OH' \rightleftarrows H_2O$, however, is all but complete, for water is hardly ionized at all (p. 331). The materials on whose interaction with the Cl' and $Na^{\cdot}$, respectively, the maintenance of molecules HCl and NaOH depends, being thus removed, the dissociation of the acid and base promptly brings itself to completion, and the left sides of the equations vanish. Practically all the hydrion and hydroxyl become water. The Cl' and $Na^{\cdot}$, however, if the solution is now semi-normal, unite to the extent of 0.266 only (p. 331). If it is more dilute, this union forms a still smaller factor in the whole change. Practically it is negligible. Now all that has been said of this acid and base will apply *mutatis mutandis* whenever any active, highly ionized acid and base come together. Thus we may write **one simple equation for all neutralizations of active acids and bases**:

$$H^{\cdot} + OH' \rightarrow H_2O,$$

without omitting anything essential.

The ions of a salt are always left over from the main action, and may be brought together, in turn, by evaporation (*cf.* p. 341).

The equations as commonly written:

$$NaOH + HCl \rightarrow NaCl + H_2O,$$
$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O,$$

apply to the interactions when water is absent. If used for neutralization in dilute solution, it must be understood that they condense two changes into one equation. The formation of water comes first, that of the salt afterwards. Sometimes neutralization is wholly misconstrued by the supposition being made that it occurs in consequence of a great tendency to salt formation.

It will be seen that neutralization is the precise reverse of hydrolysis (pp. 181, 344). The former being almost always nearly complete, the latter must be, as a rule, very slight.

Indicators. — Indicators are substances which, in presence of certain other substances, assume a very deep color, or change sharply from one deep color to another. Thus, phenolphthalëin (p. 349) is colorless in presence of acids (*i.e.*, hydrion), and red (when dilute pink) in presence of alkalies (*i.e.*, hydroxidion). Litmus, again, is red with acids, and blue with alkalies. The change of color depends upon a chemical interaction in each case, but since indicators are chosen for their strong coloration, the quantity of the acid or base used up in changing the tint of the trace of the indicator is so small as to be negligible.

The common indicators are:

Phenolphthalëin, $C_{14}H_{10}O_4$, a colorless substance and very feeble acid. It is not perceptibly dissociated into its ions:

$$C_{14}H_{10}O_4 \text{ (colorless)} \leftrightarrows C_{14}H_9O_4' \text{ (red)} + H^{\cdot},$$

and in neutral or acid solutions is, therefore, without visible color. When a base is added gradually to an acid containing some of this indicator, the acid is first neutralized. Then, and not till then, the slightest excess of hydroxidion unites with the trace of hydrion from the phenolphthalëin, the above equilibrium is displaced forwards, and a visible amount of the red negative ion is formed:

$$\begin{array}{llll} C_{14}H_{10}O_4 \text{ (colorless)} & \leftrightarrows C_{14}H_9O_4' \text{ (red)}^* & + \ H^{\cdot} & \multirow{2}{*}{} \\ NaOH & \leftrightarrows Na^{\cdot} & + \ OH' & \end{array} \Big\} \leftrightarrows H_2O.$$

This indicator shows the presence of an excess of alkali most sharply when the alkali is an active one like sodium hydroxide, and should, therefore, be employed only with strong bases. With a weak base like ammonium hydroxide, a considerable excess must often be used before the color appears.

Litmus is a natural dyestuff of unknown chemical structure. Doubtless, however, one of its colors is that of the molecule, and the other that of the ion.

Methyl orange, $(CH_3)_2NC_6H_4.N:N.C_6H_4SO_3Na$, is a complex organic compound which gives, in acid solution, a red and in alkaline solution a yellow color.

Congo red is the sodium salt of an acid of complex structure (see Dyes). In neutral or alkaline solutions it is red; with acids it turns

* The ion has this composition, but, in reality, has a different chemical structure from the corresponding part of the original molecule. An internal rearrangement, not representable in the equation, accompanies the dissociation. The same remark applies to the other indicators.

blue. Paper dipped in Congo red differs from litmus paper in that it shows gradations in color, the blue being much more distinct with an active acid than with a relatively weak one like acetic acid (p. 347). Litmus paper is equally red with all acids save the very feeblest.

Some special indicators have been mentioned. Thus, starch emulsion is used for recognizing the presence of traces of iodine (p. 235). Potassium permanganate is itself so strongly colored that it is its own indicator (p. 307).

Neutralization of Little Ionized Substances. — When concentrated solutions are employed, or acids and bases which are but little ionized are involved, the mechanism of the change is still the same in all respects. The only difference is that, since the acid or base is not fully ionized to start with, its molecules must dissociate progressively, in proportion as the hydrogen ions pass into combination. All the hydrogen and hydroxyl capable of forming ions will pass through that stage and ultimately become water before the solution can reach the neutral condition.

From this it will be seen that the *activity* of acids and bases cannot be measured by the *quantity* of base or acid required to neutralize them. The full amount required by the equation is always needed in every case. This is because neutralization uses up the hydrion or hydroxidion *at once*, and so permits the rapid generation of a fresh supply. The concentration of one of these ionic materials can only be measured by some action which uses it up slowly or not at all, so that ionic double decompositions are excluded. In the action of metals on acids (p. 347) and in determining conductivity (p. 325) the consumption of the ions is slow, and hence the measurement can be made in these cases. Actions which consume no ions at all are also known, and are used in measuring activity (see Carbohydrates and esters).

When the acid or base is but little soluble in water, as when zinc hydroxide is treated with a dilute acid, one other link is added to the network of equilibria. The acid proceeds to interact with the small dissolved part of the base. As this is disposed of, solution goes on progressively, and, through a train of equilibria:

$$Zn(OH)_2 \text{ (solid)} \leftrightarrows Zn(OH)_2 \text{ (diss'd)} \rightleftarrows Zn^{\cdot\cdot} + 2OH',$$

the supply of hydroxidion is maintained until all the molecules of the base, solid and dissolved, are used up and the action is completed. Heating hastens these, as it does all other changes.

If acid and base are alike insoluble, it is best, if the production of the salt is the ultimate object, to fuse the materials together at a high temperature.

Thermochemistry of Neutralization. — The above interpretation of the phenomena of neutralization is confirmed by many facts. Thus a considerable amount of heat is liberated in neutralization. Now, when **active acids** (p. 347) **and bases** (p. 349) **in dilute solution** are concerned, it is found that the **quantities of heat** for the neutralization of the same amount of hydrion, or hydroxidion, are **always the same**, namely, 13,700 cal. for equivalent weights. If the action consisted primarily in the formation of a different salt from every pair, we should expect the heat liberated to be different. Thus, the heats of formation of dry potassium chloride and dry sodium iodide are 10,120 cal. and 7030 cal., respectively. But the heats of formation of their solutions by neutralizing the proper acids and bases are identical. If, however, in such cases, neutralization consists always simply in the formation of water, we should expect the quantities of heat liberated to be identical, as, in fact, they are:

$$H^{\cdot} + OH' \rightarrow H_2O + 13{,}700 \text{ cal.}$$

We are confirmed in these conclusions when we employ concentrated solutions, or use less completely ionized, or insoluble acids and bases for neutralization. With such substances,—and they are in the majority,—the heats of neutralization are not alike, but different in every case. Thus, for dilute solutions of sodium hydroxide and hydrofluoric acid, the latter a slightly ionized soluble acid, the thermochemical equation is as follows:

$$NaOH + HF \rightarrow H_2O + NaF + 16{,}270 \text{ cal.}$$

Since the sodium fluoride is fully ionized, the only difference between this case and the preceding one is that the hydrogen fluoride is largely in the *molecular* condition to start with, and that here, in addition to the union of hydrogen and hydroxyl ions, we have a continuous dissociation of the hydrofluoric acid accompanying the neutralization. The fact that here the heat produced is much greater than before, shows that the dissociation of this acid is associated with the *production* of heat (*cf.* pp. 260, 330). When the same base is used with hypochlorous acid, the divergence is in precisely the opposite direction and about the same in amount:

$$NaOH + HClO \rightarrow H_2O + NaClO + 9840 \text{ cal.}$$

Here again the salt produced, sodium hypochlorite, is fully ionized, so that the diminished evolution of heat must be due to the fact that the feebly ionized hypochlorous acid absorbs part of the heat of neutralization in passing into the ionic condition. Applying this to bases, we find that the neutralization of ammonium hydroxide, a feebly ionized base, with any active acid, gives a heat of neutralization below the normal:

$$NH_4OH + HCl \rightarrow H_2O + NH_4Cl + 12{,}200 \text{ cal.}$$

Here again the salt produced is fully ionized. Thus the ionization of the ammonium hydroxide must have consumed an appreciable part of the heat of neutralization which would otherwise have reached the normal figure of 13,700 calories.

Volume Change in Neutralization. — When the volumes of the solutions of *active* acids and alkalies are carefully measured before being mixed, and compared with the volume of the neutral mixture, a contraction is always found to have occurred. When one liter of a normal solution of each substance is taken at starting, the volume of the mixture is always 20 c.c. greater than that of the component liquids. When less highly ionized acids and bases are used, the alteration in volume is irregular, since it is affected by the occurrence of other changes than the mere union of hydrion and hydroxidion.

Mixed Ionogens and Double Salts.

As a rule, a univalent ion, such as chloranion (ClO_3'), unites with one kind of cation and gives but one kind of salt (*cf.*, however, p. 242). The result is called a **neutral** or **normal salt**, as $KClO_3$ or $NaClO_3$. The acid, chloric acid, is called a **monobasic acid**, for its molecule reacts with but one molecule of a base. The possibilities are more numerous, however, with an ion of higher valence. Thus:

Carbonanion May Give:	Calcion May Give:
H_2CO_3, the acid,	$Ca(OH)_2$, the base,
Na_2CO_3, a neutral salt,	$CaCl_2$, a neutral salt,
$NaHCO_3$, an acid salt,	$Ca(OH)Cl$, a basic salt,*
$NaKCO_3$, a mixed salt,	$CaCl(OCl)$, a mixed salt.

Carbonic acid is a di-basic acid, and calcium hydroxide a di-acid base. The last two compounds of each set are **mixed ionogens**. Their characteristic is that they contain more than two kinds of radicals and break up in solution, giving more than two kinds of ions.

Acid Salts. — The acid salts are obtained by using half that quantity of the base which would be required fully to neutralize the acid, and evaporating the resulting solution:

$$NaOH + H_2SO_4 \leftrightarrows H_2O \uparrow + NaHSO_4.$$

With a monobasic acid, say hydrochloric acid, this treatment gives simply a mixture of the normal salt and the free acid, and not a single substance.

* This particular basic salt has not been isolated in a pure state.

Acid salts are also formed by the interaction of other salts with an excess of the acid (pp. 178, 179, 227).

The **acid salt** is intermediate in composition between the acid itself and the normal salt. All of the hydrogen of the acid has not been displaced by the metal. It is named an acid salt on account of its composition, but is not necessarily acid in its reaction towards litmus. That depends on whether its solution contains a sufficient amount of hydrion to affect indicators. Sodium hydrogen sulphate gives the ions $Na^{\cdot}$ and HSO_4', but, even in moderately dilute solution, the latter ion is further dissociated into $H^{\cdot}$ and SO_4'' to a large extent (p. 346). Its solution is therefore acid in truth. On the other hand, sodium hydrogen carbonate, $NaHCO_3$, derived from carbonic acid, H_2CO_3, gives the ions $Na^{\cdot}$ and HCO_3', and the amount of hydrion formed by the latter is too small to be detected by indicators. This acid salt gives therefore a solution which is actually neutral to litmus.*

Basic Salts. — Corresponding to the acid salts we have also basic salts, about which statements parallel to the above might be made. Thus, from sodium hydroxide but one salt can be formed. With lead hydroxide, $Pb(OH)_2$, however, the displacement of one hydroxyl by a negative radical, without the disturbance of the other, is conceivable and can be achieved. The half-chloride, for example, is called lead oxychloride ($Pb(OH)Cl$). The basic salts are usually insoluble in water, and therefore as a rule do not exhibit the basic reaction with litmus.

Mixed Salts. — So-called mixed salts, like sodium-potassium carbonate $KNaCO_3$, (see Silicates), may be obtained by half neutralizing the acid with the calculated amount of one base and then completing the operation with the other. Corresponding treatment will give mixed salts of a di-acid base.

It will be seen that $2KNaCO_3$ is equivalent to K_2CO_3,Na_2CO_3, and that $2CaCl(OCl)$ is equivalent to $CaCl_2,Ca(OCl)_2$. Since we have as yet no general means of determining the molecular weights of solids, there is no generally applicable way of deciding which formula is preferable (see, however, Bleaching powder, p. 266, and under Calcium). In solutions of these salts the ions which are found might come from a

* Because of hydrolysis (p. 344), the solution of the "neutral" salt, sodium carbonate Na_2CO_3, is actually *alkaline* in reaction. The terms "acid," "basic," and "neutral," applied to salts, refer simply to the composition and ignore the behavior.

substance possessing either of the alternative formulæ, so that no light is thrown on the question by this means. Thus, most compounds of this kind, with the exception of acid and basic salts,* are considered to be molecular compounds (p. 123) of two salts and are classed as **double salts**.

Double Salts. — Substances similar to ferrous-ammonium sulphate $FeSO_4,(NH_4)_2SO_4,6H_2O$, are very numerous. Because their formulæ can be written so as to show two complete salts, and because they are easily formed by crystallization from a solution containing both salts, they are called **double salts**. In solution they are resolved into their constituent salts, and these, in turn, are ionized. Almost always the acid radicals are identical (see, however, Kainite).

Each kind of ion of a double salt exhibits its own properties, irrespective of the nature of the numerous substances, ionic and otherwise, which are present. Hence, when a solution of a particular ionic material is required, solutions of such bodies are often used instead of those of simpler ones, if for any reason the substitution is convenient. The choice of the complex compound must be made in such a way that the other ions shall not interfere with that particular reaction of one of them which is in question.

The class of bodies known as *salts of complex acids* (*q.v.*) are ionized like ordinary salts and not like double salts.

Kinds of Ionic Chemical Change.

Five distinct varieties of chemical change are characteristic of ionic materials. These are: (1) Disunion or combination of ions, (2) displacement of the material of one ion by another substance, (3) destruction or formation of a compound ionic material, (4) change in the charges of two ionic materials, (5) charge or discharge of two ionic materials, electrically. Every one of these kinds of action has been illustrated, some of them very frequently, in the present and foregoing chapters.

Disunion and Combination of Ions. — This sort of change is illustrated every time an ionogen is dissolved in water (disunion) or a solution of such a substance is evaporated (combination). Both of the

* The formulæ of basic salts even are often written as if they were molecular compounds, as $Cu(OH)_2,CuCl_2$, or even $CuO,CuCl_2,H_2O$, in place of $Cu(OH)Cl$ (see Copper).

directions of this sort of change occur also to a greater or less extent whenever solutions of two ionogens are mixed. In the latter case:

(1) Two salts give two salts (pp. 337–341).
(2) An acid and salt give a salt and an acid (p. 349).
(3) A base and salt give a salt and a base (p. 350).
(4) An acid and base give water and a salt (neutralization).

(1) is complete only when at least one product is insoluble. (2) and (3) are complete when at least one product is little ionized or insoluble or both. (4) is almost always complete because water is generally less ionized than any other substance in the system.

Displacement of One Ion: Electromotive Series of the Metals. — When zinc, aluminium, and other metals are placed in a dilute acid, hydrogen is liberated (pp. 95 and 346):

$$Zn + 2H^{\bullet} \rightarrow Zn^{\bullet\bullet} + H_2.$$

This action takes place with all acids, because it concerns in reality only the hydrion in the solution. Its speed for any one metal depends on the concentration of hydrion (p. 347). Similarly, fluorine displaces chlorine from chloridion (p. 342), chlorine displaces bromine from bromidion (p. 228):

$$Cl_2 + 2Br' \rightarrow 2Cl' + Br_2,$$

and bromine displaces iodine from iodidion (p. 236). Each of these actions is independent of the nature of the other ion which accompanies the one undergoing change.

The same sort of displacement occurs with all positive ions. Thus, zinc will not only displace hydrogen, but also other metallic elements, like iron, lead, copper, and silver, from the ionic condition in solutions of their salts. Lead, in turn, will displace copper and silver, but not zinc or iron. Copper will displace silver. Thus the metals can be set down in an order such that each metal displaces those following it in the list and is displaced by those preceding it. This list (see next page) is known as the **electromotive series** of the metals, because in electrolysis of normal solutions of their salts, the electromotive force of the current required to deposit each metal (*cf.* p. 324) is less than that for the metal preceding in the list (see Electromotive chemistry).

This list embodies many facts in the behavior of the metals, and

should be kept in mind as furnishing a key to the actions in which a *free metal* is used or produced. For example, the chemical activity of the free metals places them in the same order. The earliest ones rust much more readily in air than do the later ones. Those following copper do not rust. Conversely, the oxides of the metals down to and including manganese, when heated in a stream of hydrogen, may give lower oxides, but are not completely reduced. The oxides of cadmium and succeeding metals are easily reduced. The oxides of mercury and the last four metals are decomposed by heating alone. The relations of the metals in respect to combination with elements other than oxygen are similarly expressed by the arrangement in this table.

Electromotive Series of the Metals.

Alkali metals (*q.v.*)
Alkaline earth metals (*q.v.*)
Magnesium
Aluminium
Manganese
Zinc
Chromium
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
Hydrogen
Arsenic
Copper
Antimony
Bismuth
Mercury
Silver
Palladium
Platinum
Gold

The position of hydrogen is particularly significant. It will be noted that none of the metals preceding hydrogen are found free in nature as ordinary minerals,* while all of the metals succeeding hydrogen, although occurring to some extent in combination, are found also free. The explanation of this is that, by prolonged action upon ordinary water, containing, as it must, carbonic acid and other sources of hydrogen ions, the metals preceding hydrogen must eventually displace hydrion and pass into some form of combination (*cf.* p. 346). The metals following hydrogen do not displace hydrion and are much less affected by the agencies which are most active in the chemical transformation of minerals. Hence they often remain in the free state.

The negative ions can be arranged in order in a similar way.†

* Free lead and tin do occur as rare minerals. Iron, with a little cobalt and nickel, constitutes many meteoric masses.

† To avoid a common misconception, it must be noted that the electromotive series has no bearing on the tendency of one radical to dislodge another in double decompositions. The place of an element in the E.M. series defines its relative activity *when free*, and has to do only with actions where *one free element displaces* (p. 99) another. The influences which determine a double decomposition (*cf.* pp. 180, 257–260) have little to do with the chemical activity of the compounds concerned (p. 350), and nothing at all to do with that of the free elements, for these, in fact, are not present at all (see Halides of silver).

Destruction or Formation of a Compound Ion. — The destruction of a compound ionic material is observed in the action of any reducing agent, such as hydrogen peroxide (p. 307), upon a dilute solution of a permanganate. The compound ion MnO_4' gives by reduction $Mn^{\cdot\cdot}$ and water. It was also encountered (p. 278) in the reduction of IO_3' by hydriodic acid, in which free iodine and water were formed:

$$H^{\cdot} + IO_3' + 5H^{\cdot} + 5I' \rightarrow 3H_2O + 3I_2.$$

The converse occurs when potassium cyanide is added in excess to a solution of a salt of silver. First, silver cyanide is precipitated, and then this compound unites with the excess of cyanidion:

$$Ag^{\cdot} + NO_3' + K^{\cdot} + NC' \rightleftarrows K^{\cdot} + NO_3' + AgNC\downarrow,$$
$$K^{\cdot} + CN' + AgCN\uparrow \rightarrow K^{\cdot} + Ag(CN)_2'.$$

The product is the soluble potassium argenticyanide. It is a salt of the *complex acid* $HAg(CN)_2$, and not a double salt (p. 360). It does *not* decompose into potassium and silver cyanides and their ions when in solution, for the second action, above, is not appreciably reversible.

Change in the Charges of Two Ions. — A reduction in the charge in two ions probably occurs in the preparation of chlorine (p. 171). The decomposition of the manganese tetrachloride, if it is indeed formed, takes place by the simultaneous discharge of two equivalents of electricity from the quadrivalent manganese ion and two ions of chloridion:

$$Mn^{\cdot\cdot\cdot\cdot} + 4Cl' \rightarrow Mn^{\cdot\cdot} + 2Cl' + Cl_2.$$

Both this sort of change and its converse are common with ions of metals such as iron and tin (*q.v.*), which have more than one valence.

Charge and Discharge of Two Ions, Electrically. — Discharge of ions is brought about in every electrolysis (p. 318). Thus, when hydrochloric acid is decomposed by the current, we have:

$$2\overset{+}{H} + 2\ominus \rightarrow H_2 \quad \text{and} \quad 2\overset{-}{Cl} + 2\oplus \rightarrow Cl_2.$$

The converse takes place when the polarization current (p. 324) is allowed to flow. Both charge and discharge occur in every simple battery, as when zinc dissolves in dilute sulphuric acid to give zinc sulphate (p. 346):

$$Zn + 2\oplus \rightarrow \overset{++}{Zn} \quad \text{and} \quad 2\overset{+}{H} + 2\ominus \rightarrow H_2.$$

The creation of the positive charges in the former of the two equations leaves the rod of zinc negatively charged, that of the negative charges in the latter renders the platinum wire positive.

Two or More Kinds of Ionic Action Simultaneously. — In the interaction of iodic acid and hydrogen iodide, both the decomposition of a compound ion (IO_3') and the change in charge on other ions (I' giving I_2, and $H^{\cdot}$ giving water) occur simultaneously. Complications of this kind are not uncommon.

Non-Ionic Modes of Forming Ionogens.

While ionogens may always be made by the union of the proper ions, they must nevertheless, in the absence of the solvent, be regarded as chemical substances which may be constructed out of their constituents without reference to the ionic plane of cleavage. Thus we have incidentally observed many ways in which acids, bases, and salts may be prepared that do not involve a union of the constituent ions and are probably not ionic.

Acids and Bases. — Oxygen acids can almost all be prepared from the anhydrides, which are not ionogens, and water. Phosphoric acid, sulphurous acid (p. 71), hypochlorous acid (p. 268), and many other acids are so formed. The hydrogen halides are all producible by union of the constituent elements. Many acids are formed from others when the latter are heated; for example, chloric acid from hypochlorous acid and phosphoric from phosphorous acid (*q.v.*).

Bases are formed by the union of oxides of metals with water (p. 119).

Salts. — The dry ways of forming salts are very numerous. Thus, many are formed by direct union of the elements, as in the case of chlorides (p. 175), sulphides (p. 12), and other simple salts. Many are made by reduction or oxidation from other salts, as potassium chloride from potassium chlorate (p. 65), or potassium perchlorate from the latter (p. 275). Often a reducing or an oxidizing agent is used, as in making potassium nitrite (*q.v.*) from the nitrate, and lead sulphate from lead sulphide (*q.v.*). Almost all oxygen salts can be obtained by the union of two oxides, as calcium carbonate (*q.v.*) from calcium oxide and carbon dioxide. Ammonium salts are formed by combination of ammonia, which is not an ionogen, with acids (p. 183).

In manufacturing salts, methods like the above, as well as those involving ionic actions, are very commonly used. In each case the cheapest and most easily accessible materials are chosen, and the least expensive operation is selected.

Neutralization is theoretically the simplest ionic way of getting a salt, because the water can be removed by mere evaporation. Yet most of the salts which are on the market are made by the use of other actions. In fact, the pure bases and acids are usually too expensive to be utilized as sources of salts.

The commonest definition of a salt, as a substance formed by the neutralization of an acid by a base, is open to many objections. It is logically defective because it does not describe what a salt is, but one method of making a salt, which is an entirely different matter. It is unfortunate in its choice amongst possible paralogisms, because neutralization is more significant as a method of forming water than as a means of preparing a salt. And finally, as we have just seen, the definition has not even the excuse of practical value, for most salts are manufactured by entirely different reactions.

Exercises. — 1. Using the data in regard to ionization (p. 330), formulate other dissociations according to the models on p. 335.

2. Explain fully (*cf.* p. 297) the effect of potassium bromide upon the ionization of cupric bromide (p. 335).

3. Give a list of all the colorless ionic substances you can think of (p. 337).

4. Formulate fully, according to the diagram on p. 340, the precipitation of barium sulphate (p. 342), of silicic acid from sodium silicate (p. 350), of zinc hydroxide from zinc sulphate (p. 350), of silver chloride from silver sulphate, and the liberation of hydrogen chloride by phosphoric acid (p. 179).

5. Give a list of the specific physical and chemical properties (p. 341) of iodidion and of hydrion.

6. Formulate (p. 361) the displacement of iodine by bromine (p. 236), and of bromine by chlorine (p. 232).

7. Explain the acid reaction of ferric chloride ($FeCl_3$) solution (p. 344).

8. Name all the physical components in aqueous solutions of potassium hydroxide, hydrogen chloride, and sulphuric acid (*cf.* p. 322).

9. Name the anions and cations whose formulæ are used on p. 337.

10. Formulate (p. 361) the actions of iron and of aluminium on dilute hydrochloric acid.

11. What is the molar concentration (p. 250) of hydrion in N/10 hydrogen sulphide (p. 330) and in N/10 acetic acid, of natrion in N/2 sodium chloride, and of cuprion in N cupric nitrate?

12. Combining the models on pp. 349, 354, and 356, formulate the action of hydrochloric acid on magnesium hydroxide and on zinc hydroxide.

13. Formulate (p. 338) and discuss the action of sulphuric acid upon potassium permanganate (p. 306) and upon potassium dichromate (p. 306).

14. Formulate (p. 354) the neutralizations mentioned on p. 357.

15. What do we infer (p. 359) from the fact that the solution of sodium hydrogen sulphide (NaHS) is neutral?

16. Can you invent an interaction of two soluble salts in which both products shall be insoluble?

17. To which classes of ionic actions do those of iodine on hydrogen sulphide (p. 238), and of magnesium on cold water (p. 97), belong? Formulate the former according to the model on p. 340.

18. What metals, beside platinum, would be most likely to form suitable electrodes for an electrolytic cell (p. 324)?

19. How should you attempt to obtain (p. 363) a pure aqueous solution of the acid $HAg(CN)_2$?

20. Formulate (p. 363) the electrolysis of hydriodic acid and that of cupric sulphate, the latter between copper electrodes (p. 325).

21. Give, for each of the following, two definitions, one in terms of experimental facts, the other in terms of the ionic hypothesis: acid, base, salt, neutralization, acid salt, mixed salt.

CHAPTER XXI

SULPHUR AND HYDROGEN SULPHIDE

Occurrence. — Free sulphur is found in volcanic regions, where it is mixed with gypsum and other minerals and occupies the pores of pumice-stone. Rocky materials accompanying a mineral in this way are called the **matrix**. Here and there non-volcanic deposits, formed by the action of bacteria, have been met with, as in Louisiana and in Germany. There are many minerals, compounds containing sulphur, which are chiefly important on account of their other constituents. Sulphides of metals, such as pyrite (FeS_2), copper pyrites ($CuFeS_2$), galena (PbS), zinc-blende (ZnS), and sulphates, like gypsum ($CaSO_4$, $2H_2O$), barite ($BaSO_4$), and celestite ($SrSO_4$), are fairly plentiful. Sulphur is a constituent of albumin and other substances found in the animal body.

Manufacture. — Most sulphur is obtained by the simple process of melting it away from the accompanying volcanic rock at a low temperature. The liquid sulphur is allowed to run into wooden molds, in which it solidifies in the form of **roll sulphur**. For many purposes this sulphur is sufficiently pure. To produce the best quality it is subjected to distillation from earthenware retorts. The vapor passes into a large brick chamber and condenses upon the walls and floor in the form of a fine powder, sold as **flowers of sulphur**. When the chamber has become heated, the sulphur condenses in the form of a liquid, which is drawn off and cast in molds as before.

The greater part of the sulphur of commerce comes from Sicily, where, in 1898, 447,000 tons were manufactured against 41,000 tons elsewhere. A certain amount is obtained in Japan. It is found in California, Nevada, and Louisiana. Within the last two years the product from the last-named source has superseded Sicilian sulphur in the American market. Sulphur is popularly known as brimstone.

Some sulphur is also made from polysulphides (*q.v.*) (which give **precipitated sulphur**), from the waste products of alkali manufacture by Chance's process (*q.v.*), and from the exhausted material used in removing sulphur from illuminating-gas during its purification.

Physical Properties. — The chief physical peculiarity of sulphur is that, instead of existing in three physical states only, like water, it possesses two familiar and perfectly distinct solid forms and two different liquid states of aggregation.

1. Native sulphur is yellow, has a sp. gr. 2.06 and melts at 114.5°. It is almost insoluble in water, but dissolves freely in carbon disulphide (40 parts in 100 at 18°) and in sulphur monochloride (*q.v.*). When good crystals are found, they belong to the rhombic system (Fig. 1, p. 11). The solid sulphur obtained by evaporating a solution shows, as a rule, more perfect crystalline forms than does native sulphur, but in all other respects is identical with it. Roll sulphur is the same substance as these two, although the crystals in their growth have interfered with one another, and the mass is **crystalline**, simply, and not **well crystallized**. This variety is called, from its form, **rhombic sulphur.**

2. When a large mass of melted sulphur solidifies slowly, and the crust is pierced and the remaining liquid poured out before the whole has become solid, the interior is found to be lined with long needles. This kind of sulphur is nearly colorless and has a sp. gr. 1.96, melts at 119°, and is in all physical respects a different individual from rhombic sulphur. The crystals are long, transparent prisms, almost rectangular in section, and usually showing one large oblique face at the end. This variety of the simple substance is named, from the system to which its crystals belong, **monoclinic sulphur**.

Monoclinic sulphur can be kept only *above* 96° and below its melting-point (119°). Every recently solidified mass of sulphur is composed of it. But, below 96° the mass gradually becomes opaque, the change usually spreading from one or two points and finally affecting the whole mass. The opacity is due to the fact that the material has turned into an aggregate of small particles of rhombic sulphur, each of which occupies less space than the monoclinic sulphur from which it was formed. Conversely, rhombic sulphur can be kept only *below* 96°. When heated above this temperature, but not as high as its melting-point, it turns slowly into monoclinic sulphur. Contact with a piece of monoclinic sulphur, or mere rubbing with a hard body, will determine the point at which the transformation shall begin, and the expansion which accompanies this results in a spreading opacity as before. The delay before the change starts and the effect of rubbing and inoculation are familiar in connection with almost all changes of state (*cf.* p. 159).

Transitions, marked by definite points, like this one at 96°, are attended by similar phenomena, whether they lie between two solid states, or a liquid and a solid state (ice and water), or a gaseous and a liquid state (steam and water). Heat is given out when we pass in one direction and absorbed by passage in the other. The rate of change of vapor pressure with change in temperature (*cf.* p. 163) is different on each side of the transition point. A body which has two solid states, and, therefore, two crystalline *forms*, is said to be **dimorphous** (two-formed), and one with more than two such states **polymorphous** (see Ammonium nitrate). But this term is not intended to imply that the relation of two solid states to each other is essentially different from that of two states of different kinds, such as solid and liquid, although the term "polymorphous" is not applied to the latter.

3. When melted sulphur is heated, it undergoes another change at 160°. The formerly **pale-yellow, mobile liquid** (S_λ) suddenly becomes **dark** in color and so **viscous** (S_μ) that the vessel may be inverted without loss of material. Beyond 260° the viscidity becomes noticeably less, and at 448.5° the liquid boils and passes into sulphur **vapor.**

The sulphur thermometer thus shows many more fixed points than does the water thermometer. The latter consists of ice up to 0°, of water from 0°–100°, and of steam above 100°. The former includes rhombic sulphur up to 96°, monoclinic sulphur 96°–119°, mobile liquid (S_λ) 119°–160°, viscous liquid (S_μ) 160°–448.5°, and vapor beyond.

Insoluble, Amorphous Sulphur. — When sulphur which has been exposed to the air, and particularly sulphur to which a *trace* of iodine has been added, is boiled and then allowed *slowly* to cool, the product is crystalline and soluble in carbon disulphide, as before. But when such impure sulphur is boiled and then *suddenly chilled* by pouring into cold water, it is at first semi-fluid. After several days this *elastic sulphur*, as it is called, becomes hard. It is then found to contain rhombic sulphur mixed with a large proportion of another variety of free sulphur. This is almost insoluble in any solvent, and so may be secured by washing the mixture with carbon disulphide.

This **insoluble sulphur**, being without crystalline structure, is called also **amorphous** (Gk. ἀ priv., μορφή form) sulphur. Now amorphous bodies (see Glass) are always supercooled liquids, that is, liquids still existing as such at a temperature at which the solid, crystalline form is the stable one. They have been brought, by cooling, so rapidly

through their freezing-point (in general, transition point from one physical state to another) that crystallization has not had time to begin (*cf.* p. 144) and a general rigidity only has supervened. Now amorphous sulphur is viscous, liquid sulphur (S_μ) which, by sudden chilling, has been carried past both the transition to mobile liquid sulphur (S_λ) at 160°, and the crystallization as well, without undergoing either of these changes. It is supercooled S_μ. This accounts for the fact that it is obtainable only by rapid cooling. Often over 50 per cent of the whole may thus be supercooled. Once the mixture has been obtained by chilling, the insoluble sulphur reverts very slowly to the soluble variety, and years are required for the completion of the reversion at ordinary temperature. At 100° the reversion is completed in an hour. The capacity of the S_μ to be supercooled at all seems to depend on the presence of traces of foreign bodies. Of these, iodine is the most efficient. The sulphur dioxide or sulphuric acid produced by prolonged exposure to the air (see below) is the agent usually responsible for the supercooling. Freshly recrystallized sulphur gives no elastic sulphur and no insoluble sulphur.

Insoluble sulphur is found in flowers of sulphur and in sulphur formed by precipitation from thiosulphates (*q.v.*) in presence of acids.

Chemical Properties. — When the density of sulphur vapor is determined at low temperatures and under reduced pressures, the molecular weight corresponds closely to the formula S_8. As the temperature is raised, however, the vapor expands very rapidly, and at 800° the molecular weight is 64.2, and the formula therefore S_2. Intermediately mixtures of S_8, S_6, S_4, and S_2 exist. At higher temperatures no further dissociation seems to take place. The formula of dissolved sulphur, as measured by freezing- and boiling-point methods (p. 162), is S_8.

We do not ordinarily think of sulphur as a very active chemical substance, but this is largely due to the fact that its solid condition interferes with the attainment of close contact with the body upon which it acts. When finely divided metals, with the exception of gold and platinum (*cf.* p. 362), are rubbed together with powdered sulphur, union takes place and sulphides are produced. We have seen that sulphur when heated combines with great vigor with iron and copper, as it does indeed with most of the metals. Sulphur unites also with many of the non-metals. Thus with oxygen it produces sulphur dioxide, and even sulphur trioxide (SO_3). It unites also with

chlorine directly. When sulphur is treated with oxidizing agents *in presence of water*, no trace of sulphur dioxide (or sulphurous acid) is formed; the only product is sulphuric acid. Even free oxygen gas in the air is capable slowly of oxidizing moist powdered sulphur and producing sulphuric acid, $2S + 2H_2O + 3O_2 \rightarrow 2H_2SO_4$.*

Uses of Sulphur. — Large quantities of crude sulphur are employed for making sulphur dioxide, which is used in the manufacture of sulphuric acid, in bleaching feathers, straw, and wool, and in making alkali sulphites for employment in the bleaching industry. The manufacture of carbon disulphide consumes a considerable amount also. The purified sulphur is employed in the manufacture of gunpowder, fireworks, matches, and, by combination with rubber, of vulcanite. Flowers of sulphur is used in vineyards to destroy fungi, which it does by virtue of the traces of sulphuric acid it yields by oxidation.

Hydrogen Sulphide.

This compound is found in some mineral waters, which in consequence are known as sulphur waters. It is produced in the decomposition of animal matter containing sulphur, when air is excluded, and the distinctive odor of rotten eggs is due in part to its presence.

Preparation. — 1. Hydrogen and sulphur do not unite perceptibly in the cold. At 310° almost complete union occurs, but about 168 hours are required for the change.

2. Sulphides of metals, being salts, are acted upon more or less easily by dilute acids (p. 349), and give hydrogen sulphide. Ferrous sulphide, the least expensive of those easily affected, is generally used:

$$FeS + 2HCl \rightarrow H_2S + FeCl_2.$$

For hydrochloric acid we may substitute an aqueous solution of any active, non-oxidizing acid. A Kipp's apparatus (p. 97) is commonly employed. Since ferrous sulphide is but slightly soluble in water, the action proceeds by a rather complex series of equilibria:

$$\left.\begin{array}{r} FeS\ (solid) \leftrightarrows FeS\ (diss'd) \leftrightarrows Fe^{\cdot\cdot} + S'' \\ 2HCl \leftrightarrows 2Cl' + 2H^{\cdot} \end{array}\right\} \leftrightarrows H_2S\ (diss'd) \rightleftarrows H_2S\ (gas).$$

* The paragraph on the chemical relations of the element (see end of this chapter) should be read at this point.

The dissolved hydrogen sulphide is very feebly ionized, and maintains a smaller concentration of sulphidion (S'') than does ferrous sulphide, in spite of the comparative insolubility of the latter. Hence, the S'' formed from the FeS is continuously removed by union with the hydrion furnished by the acid, $S'' + 2H^{\cdot} \leftrightarrows H_2S$, and all the other equilibria are constantly displaced forwards on this account. The action is therefore, in essence, like neutralization (p. 354). It will be observed that the action takes place rather on account of the feeble ionization of the weak acid than by reason of the activity of the other acid. We should therefore prefer to say that the weak acid *withdraws*, and not, as is sometimes done, that the strong acid *drives* it out.

Since the action is an ionic one, the acids must be employed in dilute form. This is true especially of oxygen acids. Thus, concentrated sulphuric acid has little action upon ferrous sulphide in the cold, and when the substances are heated the oxygen of the sulphuric acid comes into play, and sulphur dioxide (*q.v.*) and free sulphur are formed.

3. Hydrogen sulphide is the invariable product of the extreme reduction of any sulphur compound. Thus, it is formed by the action of hydrogen iodide upon concentrated sulphuric acid (p. 237). Even sulphur itself is reduced by dry, gaseous hydrogen iodide:

$$2HI + S \rightarrow H_2S + I_2.$$

The action appears to be just the reverse of that which takes place in aqueous solution (p. 238), but in reality is quite different. Iodine and gaseous hydrogen sulphide will not produce free sulphur and gaseous hydrogen iodide, for this action would involve a considerable increase in energy in the system. But, in water, they do give hydrion and iodidion, for these bodies contain very much less energy than does hydrogen iodide:

$$2H^{\cdot} + S'' + I_2 \rightarrow 2H^{\cdot} + S\downarrow + 2I' \quad \text{or} \quad S'' + I_2 \rightarrow S\downarrow + 2I'.$$

Physical Properties. — Hydrogen sulphide is a colorless gas with a characteristic odor. When liquefied, it boils at $-60.4°$ (755 mm.), and in solid form melts at $-82.9°$. At 12° the liquid exerts a pressure of 15 atmospheres. The solubility in water at 10° is 360 volumes in 100, and becomes less as the temperature is raised. The gas can be driven out completely by boiling the solution (*cf.* p. 182). The

gas is very poisonous, one part in two hundred being fatal to mammals, while it is stated that one part in fifteen hundred produces death in birds.

Chemical Properties of the Gas. — When heated, the gas dissociates:

$$H_2S \rightleftarrows H_2 + S.$$

At 310° the decomposition, although very slow, affects a small but perceptible proportion of the gas before coming to rest. The dissociation, like all thermal dissociations, is accompanied by an absorption of heat and is therefore greater at higher temperatures (*cf.* p. 260).

Hydrogen sulphide forms a solid hydrate with water, $H_2S, 7H_2O$, the behavior of which resembles that of chlorine hydrate (p. 174). The vapor tension of water and the gas amount, together, to 1 atmosphere at 5°. The compound, therefore, decomposes rapidly at 5°, and more slowly at lower temperatures.

The gas burns in air, forming steam and sulphur dioxide. The temperature of the mantle of flame surrounding the gas, as it issues from a jet, being far above 310°, the gas in the interior is dissociated before it meets with any oxygen. Hence a *cold* dish held across the flame receives a deposit of free sulphur, and a part of the hydrogen also escapes unburnt. It may be remarked that dissociation of this kind probably precedes the combustion of most gaseous compounds (see Flame).

The metals, down to and including silver in the electromotive series, when exposed to the gas, quickly receive a coating of sulphide. That the gas should thus behave like free sulphur shows its instability.

This instability is shown also in the fact that its hydrogen reduces substances, such as sulphur dioxide, which are not affected by free hydrogen:

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S.$$

This action takes place much more rapidly when the gases are moist than when they are dry, and is retarded by dilution with indifferent gases (*cf.* p. 252). Native sulphur is probably produced by this action, as both of these gases are found issuing from the ground in volcanic neighborhoods. Sulphur is deposited also when hydrogen sulphide undergoes a partial combustion with a restricted supply of oxygen:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S.$$

Its formation in nature is sometimes to be accounted for in this way.

When hydrogen sulphide gas is led through concentrated, or even, simply, normal sulphuric acid, the acid is reduced, sulphur dioxide escapes, and sulphur is deposited:

$$H_2S + H_2SO_4 \rightarrow S + 2H_2O + SO_2.$$

The sulphuric acid may be written H_2O, SO_3. In furnishing SO_2, therefore, each molecule can give one unit of oxygen and therefore oxidize one molecule of H_2S (see p. 389). On account of this action the gas cannot be dried by means of concentrated sulphuric acid. Calcium chloride is likewise inapplicable, since a partial interchange takes place, resulting in the production of calcium sulphide and hydrogen chloride gas. Only a dehydrating agent, such as phosphoric anhydride, with which it cannot interact, is suitable for drying the gas.

Chemical Properties of the Aqueous Solution of Hydrogen Sulphide. — While the gas itself is not an acid, its solution in water gives a feeble acid reaction with litmus. In an aqueous solution (N/10), only .0007 (0.07 per cent) of the substance is ionized according to the equation (*cf.* p. 346):

$$H_2S \rightarrow H^{\cdot} + HS'.$$

Some S'' ions are present, but hydrosulphidion (HS') is less dissociated than is water itself, and the amount of sulphidion is therefore very small.

By the action of oxygen from the air upon an aqueous solution of hydrogen sulphide, the sulphur is slowly displaced and appears in the form of a fine white powder:

$$O_2 + 2H_2S \rightarrow 2S + 2H_2O.$$

This is an action similar to the displacement of ionic iodine by free chlorine (p. 236). On the other hand, the hydrogen may be displaced by metals, particularly the more active ones, but the small degree of ionization makes the action very slow.

The solution of the gas is a reducing agent, as its action upon iodine shows (p. 238). So, also, in presence of an acid, it removes oxygen from dichromic acid (produced by the action of an acid upon potassium dichromate):

$$K_2Cr_2O_7 + 2HCl \rightleftarrows H_2Cr_2O_7 + 2KCl \quad (1)$$
$$H_2Cr_2O_7 + 6HCl \rightarrow 4H_2O + 2CrCl_3(+ 3O) \quad (2)$$
$$(3O) + 3H_2S \rightarrow 3H_2O + 3S \quad (3)$$

Adding: $K_2Cr_2O_7 + 8HCl + 3H_2S \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3S$

The first partial equation (*cf.* p. 228) represents the regular interaction of two ionogens, but the second interaction does not take place unless an oxidizable body (here the hydrogen sulphide) is present to take possession of the oxygen which it is capable of delivering (*cf.* p. 307).

As an acid, the solution of hydrogen sulphide, sometimes known as sulphydric acid, may be neutralized by bases.

Sulphides. — As a di-basic acid (p. 358), hydrogen sulphide gives both acid and neutral (or normal) sulphides, such as NaHS and Na_2S.

The former are obtained by passing the gas in excess into solutions of soluble bases:

$$H_2S + NaOH \rightarrow H_2O + NaHS,$$

and are neutral in reaction. Their negative ion, HS′, gives practically no hydrion.

By adding to the above solution an amount of sodium hydroxide equal to that used before, and driving off the water by evaporation, the second unit of hydrogen is displaced:

$$NaOH + NaHS \leftrightarrows Na_2S + H_2O \uparrow.$$

This action is wholly reversed when dry sodium sulphide is dissolved in water, the salt being completely hydrolyzed to the acid salt:

$$\left.\begin{array}{l} Na_2S \leftrightarrows 2Na^{\cdot} + S'' \\ H_2O \leftrightarrows OH' + H^{\cdot} \end{array}\right\} \leftrightarrows HS'.$$

The HS′ gives a lower concentration of hydrion than the water, and hence uses up in its formation the ions of hydrogen produced by the latter until an amount of hydroxyl equivalent to half the sodium is formed.

Many sulphides are insoluble in water, and these may be divided roughly into three classes:

1. The sulphides of silver, copper, mercury, and some other metals are exceedingly insoluble, and, therefore, do not interact with dilute acids as does ferrous sulphide (p. 371). These may therefore be made by leading hydrogen sulphide into a solution of any of their salts:

$$CuSO_4 + H_2S \leftrightarrows CuS \downarrow + H_2SO_4.$$

The acid produced has scarcely any effect upon the sulphide, and almost no reverse action is observed.

2. The sulphides of iron, zinc, and certain other metals are insoluble in water, but not so much so as the last class. Hence they are decomposed by dilute acids, and the reverse of the above action takes place almost completely. These sulphides must therefore be made, either by combination of the elements, or by adding a soluble sulphide to a solution of a salt:

$$FeSO_4 + (NH_4)_2S \leftrightarrows FeS \downarrow + (NH_4)_2SO_4.$$

No acid is produced in this sort of interaction, and the considerable insolubility of the sulphide of iron or zinc in water renders the change nearly complete.

3. The sulphides of barium, calcium, and some other metals (*q.v.*), although insoluble in water, are hydrolyzed by it, and give soluble products (see p. 604):

$$2CaS + 2H_2O \leftrightarrows Ca(OH)_2 + Ca(SH)_2.$$

They may be prepared by direct union of the elements, and from the sulphates by reduction with carbon. (For the application of the above differences in solubility amongst sulphides in chemical analysis, see end of Chap. xxxvii.)

The soluble acid sulphides are oxidized in aqueous solution by atmospheric oxygen:

$$2NaSH + O_2 \rightarrow 2NaOH + 2S.$$

The sulphur is not precipitated, but combines with the excess of the sulphide, forming polysulphides (see below).

Polysulphides. — When sulphur is shaken with a solution of a soluble sulphide or acid sulphide, it dissolves, and evaporation of the solution leaves substances varying in composition from Na_2S_2 to Na_2S_5. Whether those containing less than five units of sulphur are mixtures of the pentasulphide with the ordinary sulphide (Na_2S) in different proportions, or are single substances, has not been determined.

When an acid is poured into sodium pentasulphide solution, minute spherules of rhombic sulphur are precipitated:

$$Na_2S_5 + 2HCl \rightarrow 2NaCl + H_2S \uparrow + 4S \downarrow.$$

When the order is reversed, sodium pentasulphide being thrown into concentrated hydrochloric acid, no hydrogen sulphide is evolved. **Hydrogen pentasulphide,** H_2S_5, a yellow oil, falls to the bottom of the vessel.

When purified, the compound is nearly colorless. Sulphur dissolves in it freely, giving a yellow solution. It can be kept without change when dry, but contact with water causes it to decompose into hydrogen sulphide and sulphur.

The Chemical Relations of the Element. — In combination with metals and hydrogen, sulphur is bivalent, forming compounds like H_2S, FeS, CuS, and HgS. In combination with non-metals, however, the valence is frequently greater, the maximum being seen in sulphur trioxide, where we must assume that the sulphur is sexivalent. Its oxides are acid-forming, and it is, therefore, a non-metal.

Sulphur is regarded as resembling oxygen more closely than any of the other elements *we have studied so far*. Both unite directly with most metals and non-metals. In this they are like chlorine. But hydrogen chloride is highly ionized by water, while the hydrogen compounds of oxygen and sulphur are feebly ionized. The formulæ of the compounds of oxygen and sulphur with metals are similar, CuO and CuS, NaOH and NaSH, and so forth, but this is in part due merely to the fact that both elements are bivalent. The chemical resemblance of sulphur to selenium and tellurium (*q.v.*) is much more striking than its resemblance to oxygen.

Exercises. — 1. The freezing-point of pure sulphur is found to vary from 119° down to 114°, depending upon the temperature to which the liquid has been heated and the speed with which it has been cooled. To what should you suspect this variability to be attributable?

2. How could the decomposition of hydrogen sulphide at 310° be rendered (*a*) more complete, (*b*) less complete? Would the percentage decomposed be affected (*a*) by reducing the pressure, (*b*) by mixing the gas with an indifferent gas?

3. To what classes of ionic actions (p. 360) do the interactions of hydrogen sulphide solution and (*a*) oxygen (p. 374), (*b*) acidified potassium dichromate (p. 374), (*c*) sodium hydroxide (p. 375), (*d*) iodine (p. 372), belong?

4. Why is normal sodium sulphide only half hydrolyzed by water?

CHAPTER XXII

THE OXIDES AND OXYGEN ACIDS OF SULPHUR

FOUR oxides of sulphur, represented by the formulæ S_2O_3, SO_2, SO_3, and S_2O_7, are known. Of these, however, the first and the last are much less familiar substances than the other two. The dioxide and trioxide of sulphur are not only important in themselves, but their relation to the acids H_2SO_3 and H_2SO_4, which may be obtained from them by the addition of water, makes them doubly so to the chemist.

Preparation of Sulphur Dioxide. — When sulphur burns in air or oxygen, sulphur dioxide is produced (p. 67). While some of the sulphur dioxide used in commerce is prepared in this manner, the larger part is probably obtained by the **roasting** of sulphur ores. Pyrite (FeS_2), for example, which is a familiar yellow, metallic-looking mineral, burns when it has been raised to the kindling temperature, on account of the large amount of sulphur which it contains:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2.$$

It should be noted in passing, that **heating** and **roasting** are distinct processes in chemistry. The latter term always assumes the access of the air and employment of its oxygen; the former, in the absence of modifying words, assumes the exclusion or the chemical indifference of the air.

Sulphur dioxide is also set free by the action of acids upon sulphites. Sulphuric acid and a strong solution of sodium sulphite may be used:

$$\left.\begin{array}{l} Na_2SO_3 \leftrightarrows 2Na^{\cdot} + SO_3'' \\ H_2SO_4 \leftrightarrows SO_4'' + 2H^{\cdot} \end{array}\right\} \leftrightarrows H_2SO_3 \leftrightarrows H_2O + SO_2 \text{ (diss'd)} \rightleftarrows SO_2 \text{ (gas)}.$$

The sulphurous acid being only moderately ionized, its molecules are formed in considerable amount. Being also very unstable, it decomposes spontaneously into water and sulphur dioxide, and the latter escapes when sufficient water for its solution is not present.

In the laboratory, sulphur dioxide is frequently made by the reduction of concentrated sulphuric acid. Copper is the metal most commonly employed, because by its means very pure sulphur dioxide can be obtained. More active metals, such as iron and zinc, although cheaper, cannot be used, since they reduce the sulphuric acid to hydrogen sulphide. The undiluted hydrogen sulphate consists entirely of molecules, and, at the high temperatures at which alone the action is vigorous, is an oxidizing agent (*cf.* p. 97). A part of it loses oxygen to form water with the hydrogen of another molecule:

$$H_2SO_4 \rightarrow H_2O + SO_2 (+O) \quad (1)$$
$$\underline{(O) + H_2SO_4 + Cu \rightarrow H_2O + CuSO_4} \quad (2)$$
$$2H_2SO_4 + Cu \rightarrow 2H_2O + SO_2 + CuSO_4$$

Some easily oxidized non-metals, such as carbon and sulphur, act in the same way:

$$C + 2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + CO_2,$$
$$S + 2H_2SO_4 \rightarrow 2H_2O + 3SO_2.$$

Physical Properties. — Sulphur dioxide is a gas possessing a penetrating and characteristic odor. This is frequently spoken of as the "odor of sulphur," but it should be remembered that sulphur itself has scarcely any smell at all. The weight of the G.M.V. of the gas (65.55 g.) shows it to be more than twice as heavy as air. The critical temperature is 156°. By means of a freezing mixture of ice and salt, the gas is easily condensed to a transparent, mobile fluid, which boils at $-8°$. At 20° the vapor tension of the liquid is 3.25 atmospheres. The liquid may be frozen to a white solid, melting at $-76°$. It ionizes substances dissolved in it as well as does water. The solubility of the gas in water, 5000 volumes in 100, is very great. Unlike solutions of the hydrogen halides (p. 182), however, the liquid is completely freed from the gas by boiling.

Chemical Properties. — Sulphur dioxide is stable, being decomposed only by the use of a very high temperature.

It unites with water to form sulphurous acid, H_2SO_3. Although the gas itself sometimes receives this name, it is not acid: it is simply the anhydride (p. 71) of the acid.

Since the maximum valence of sulphur is 6, sulphur dioxide, in which but four of the valences of sulphur are used, is **unsaturated**. It is therefore still able to combine directly with suitable elements,

such as chlorine and oxygen. When it is mixed with chlorine in sunlight, a liquid, sulphuryl chloride SO_2Cl_2 is produced.

Liquefied sulphur dioxide is now sold in tin cans, and is employed for bleaching straw, wool, and silk. As a disinfectant it has been displaced to a large extent by formaldehyde.

Preparation of Sulphur Trioxide. — Although the formation of sulphur trioxide SO_3 is accompanied by the liberation of much heat, sulphur dioxide and oxygen, even when heated together, unite very slowly. Ozone, however, combines with the former readily.

The interaction of sulphur dioxide and oxygen is hastened by many substances, such as glass, porcelain, ferric oxide, and, more especially, finely divided platinum, which remain themselves unchanged and simply act as catalytic agents. The "contact process," as this is called, has been rendered available for the commercial manufacture of sulphur trioxide by Knietsch (1901). The chief features of the process are: (1) The complete removal of arsenious oxide and other impurities derived from the burning of crude pyrite, the minutest traces of which poison the catalytic agent and soon render it absolutely inoperative. (2) The preliminary passage of the cold mixture of gases over the outside of the pipes containing the contact agent. This removes part of the heat generated by the action, $SO_2 + O \rightleftarrows SO_3 + 22{,}600$ cal., going on inside, and keeps the temperature of the interior at 400°. Below 400° the union is too slow; above 400°, being reversible, it is incomplete. At 400°, 98–99 per cent of the materials unite; at 700°, only 60 per cent, at 900° none. Twice the quantity of oxygen theoretically needed is employed. The vaporous product is condensed by being led into 97–99 per cent sulphuric acid, and the concentration of the liquid is constantly maintained at this point by the regulated influx of water. The trioxide is thus chiefly used for immediate conversion into sulphuric acid.

Formerly sulphur trioxide was obtained by the distillation of impure ferric sulphate, $Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$. It may also be prepared by repeated distillation of concentrated sulphuric acid with a powerful drying agent, like phosphoric anhydride.

Physical Properties. — Sulphur trioxide SO_3 is, at ordinary temperatures, fluid. The crystals, obtained by cooling, melt at 14.8°. The liquid boils at 46°, and is, therefore, exceedingly volatile at ordi-

nary temperature. It fumes strongly when exposed to the air, in consequence of the union of the vapor with moisture and the production of minute drops of sulphuric acid.

A white crystalline variety of the substance, which in appearance closely resembles asbestos, is obtained when a trace of water has gained access to the oxide. It is a polymer (p. 242) of the above liquid, having twice its molecular weight, and therefore the formula $(SO_3)_2$. When heated at 50° this polymer begins to dissociate and passes into vapor of SO_3 without melting. This white solid is the more stable and more familiar form of the trioxide.

Chemical Properties.— The vapor of sulphur trioxide dissociates above 400° into sulphur dioxide and oxygen.

Sulphur trioxide is not itself an acid, but it is the anhydride of sulphuric acid. When placed in water it unites vigorously, causing a hissing noise due to the steam produced by the heat of the union. In consequence of its great tendency to combine with water, the liquid variety, which is the more active, removes the elements of this substance from materials which contain them in the proper proportions. Thus paper, which is largely cellulose, $(C_6H_{10}O_5)_x$, and sugar, $C_{12}H_{22}O_{11}$, are charred by it, and carbon is set free.

Just as sulphur trioxide unites with water to give hydrogen sulphate, so it combines vigorously with many oxides of metals, producing the corresponding sulphates:

$$H_2O + SO_3 \leftrightarrows H_2SO_4, \qquad CaO + SO_3 \rightarrow CaSO_4.$$

The union of an oxide of a non-metal with the oxide of a metal, in this fashion, is a general method of obtaining salts (*cf.* p. 364).

Oxygen Acids of Sulphur.— Sulphurous and sulphuric acids have been mentioned frequently already. Next to them in importance come thiosulphuric acid and persulphuric acid. The compositions of the acids show their relationships:

Hyposulphurous acid,	$H_2S_2O_4$	Thiosulphuric acid,	$H_2S_2O_3$
Sulphurous acid,	H_2SO_3	Persulphuric acid,	$H_2S_2O_8$.
Sulphuric acid,	H_2SO_4		

Thiosulphuric acid (Gk. θεῖον, sulphur) is so named because it contains one unit of sulphur in place of one of the units of oxygen of sulphuric acid. Besides the above we have also: Dithionic acid $H_2S_2O_6$,

trithionic acid $H_2S_3O_6$, tetrathionic acid $H_2S_4O_6$, and pentathionic acid $H_2S_5O_6$.

On account of its commercial importance and the interest attaching to its method of manufacture and to its properties, we may first discuss sulphuric acid. We shall then be able to dispose of the remaining acids in a much briefer fashion.

Sulphuric Acid.

Although salts of sulphuric acid, such as calcium sulphate, are exceedingly plentiful in nature, the preparation of the acid by chemical action upon the salts is not practicable. The sulphates, indeed, interact with all acids, but the actions are reversible. The completion of the action by the plan used in making hydrogen chloride (p. 180), involving the removal of the sulphuric acid by distillation, would be difficult on account of the involatility of this acid. It boils at 330°; and active acids, less volatile still, which might be used to liberate it, do not exist. We are therefore compelled to build up sulphuric acid from its elements.

The union of sulphur dioxide and oxygen by the contact process, and combination of the trioxide with water (p. 380), is the best method for making a highly concentrated acid. For obtaining ordinary "oil of vitriol," however, an entirely different plan is still used extensively.

History of Sulphuric Acid Manufacture. — Impure forms of sulphuric acid have been known for many centuries. In the fifteenth century it was made by distilling ferrous sulphate with sand. The product, however, contained much water and sulphur dioxide. The first successful preparation of the substance commercially was made by Ward at Richmond-on-the-Thames (1758). The process consisted in burning a mixture of sulphur and saltpeter (KNO_3) in a ladle suspended in a large glass globe partially filled with water. The gases which were evolved contained large quantities of sulphur dioxide and oxides of nitrogen, which by interaction with atmospheric oxygen and water (see below) produced the sulphuric acid. The solution which was obtained, although it could be prepared of any desired concentration by the burning of a sufficient number of charges, was far from pure and was expensive, bringing thirteen shillings ($3.25) per pound. Subsequently a chamber lined with lead was substituted

for the glass vessel. This reduced the price to about two shillings and sixpence ($0.60) per pound. The same principles are used in the modern "chamber process."

Chemistry of the Chamber Process. — The gases, the interactions of which result in the formation of sulphuric acid, are: water vapor, sulphur dioxide, nitrous anhydride N_2O_3 (*q.v.*), and oxygen. These are obtained, the first by injection of steam, the second usually by the burning of pyrite, the third from nitric acid, and the fourth by the introduction of air. The gases are thoroughly mixed in large leaden chambers, and the sulphuric acid condenses and collects upon the floors. In spite of elaborate investigations, instigated by the extensive scale upon which the manufacture is carried on and the immense financial interests involved, some uncertainty still exists in regard to the precise nature of the chemical changes which take place. According to Lunge the greater part of the product is formed by two successive actions, the first of which yields a complex compound that is decomposed by excess of water in the second:

$$H_2O + 2SO_2 + N_2O_3 + O_2 \rightarrow 2SO_2\begin{matrix}\nearrow O-H \\ \searrow O-NO\end{matrix} \qquad (1)$$

The group —NO is found in many compounds. Here, if it were displaced by hydrogen, sulphuric acid would result. Hence this compound is called *nitrosylsulphuric acid:*

$$2SO_2\begin{matrix}\nearrow O-H \\ \searrow O-NO\end{matrix} + H_2O \rightleftarrows 2SO_2\begin{matrix}\nearrow OH \\ \searrow OH\end{matrix} + N_2O_3. \qquad (2)$$

The equations (1) and (2) are not partial equations for one interaction, but represent distinct actions which can be carried out separately. In a properly operating plant, indeed, the nitrosylsulphuric acid is not observed. But when the supply of water is deficient, white "chamber crystals," consisting of this substance, collect on the walls.

The explanation of the success of this seemingly roundabout method of getting sulphuric acid is as follows: The direct union of sulphur dioxide and water to form sulphurous acid is rapid, but the action of free oxygen upon the latter, $2H_2SO_3 + O_2 \rightarrow 2H_2SO_4$, is exceedingly slow. Reaching sulphuric acid by the use of these two changes, although they constitute a direct route to the result, is not feasible in practice. On the other hand, both of the above actions, (1) and (2), happen to be much more speedy, and so, by their use,

more rapid production of the desired substance is secured at the expense of a slight complexity. It may be added that the heat finally given out in the formation of one formula-weight of sulphuric acid is exactly the same in amount whether nitrous anhydride intervenes or not (*cf.* p. 78).

The progress of the first action is marked by the disappearance of the brown nitrous anhydride, and, on the introduction of water, the completion of the second results in the reproduction of the same substance. It would thus seem as if the nitrous anhydride should take part an indefinite number of times in these changes and so facilitate the conversion of an unlimited amount of sulphur dioxide, oxygen, and water into sulphuric acid, without impairment of its quantity. In practice, however, certain subsidiary actions take place, such as, for example, the reduction of some nitrous anhydride to nitrous oxide (N_2O), which permanently remove a part of the material from participation in the cycle.

The supply of nitrous anhydride is maintained by the introduction of nitric acid vapor into the chamber. This acid is secured by the action of concentrated sulphuric acid upon commercial sodium nitrate $NaNO_3$:

$$NaNO_3 + H_2SO_4 \rightleftarrows HNO_3\uparrow + NaHSO_4.$$

On account of the volatility of the nitric acid, a moderate heat is sufficient to remove it from admixture with the other substances, and its vapor is swept along with the other gases into the apparatus. The initial action which the nitric acid undergoes may be represented by the following equation:

$$H_2O + 2SO_2 + 2HNO_3 \rightarrow 2H_2SO_4 + N_2O_3.$$

We may write this in the form:

$$H_2O + 2SO_2 + H_2O,N_2O_5 \rightarrow 2H_2SO_4 + N_2O_3.$$

The two molecules of water, one actually, the other potentially, present, with the two molecules of sulphur dioxide, can furnish two molecules of sulphurous acid (H_2SO_3). The N_2O_5 in passing to the condition N_2O_3 gives up the two units of oxygen required to convert this sulphurous acid into sulphuric acid.

It should be remarked that we shall later find nitrous anhydride to be an unstable substance, which, in the gaseous form, is composed largely of the products formed by its dissociation, $N_2O_3 \rightleftarrows NO_2 + NO$.

For the purpose of understanding its present use, however, it is not necessary to consider this particular fact. The whole behaves as if it contained nothing but N_2O_3.

Details of the Chamber Process. — The sulphur dioxide is produced in a row of small furnaces *A* (Fig. 84), the structure of which depends upon the nature of the substance employed to yield this fundamental constituent of sulphuric acid. When good pyrite is used, the ore burns unassisted (p. 42), while impure pyrite and zinc-blende ZnS have to be heated, to a greater or less degree, artificially to maintain the combustion. The gases from the various furnaces pass into one long dust flue, in which they are mingled with the proper

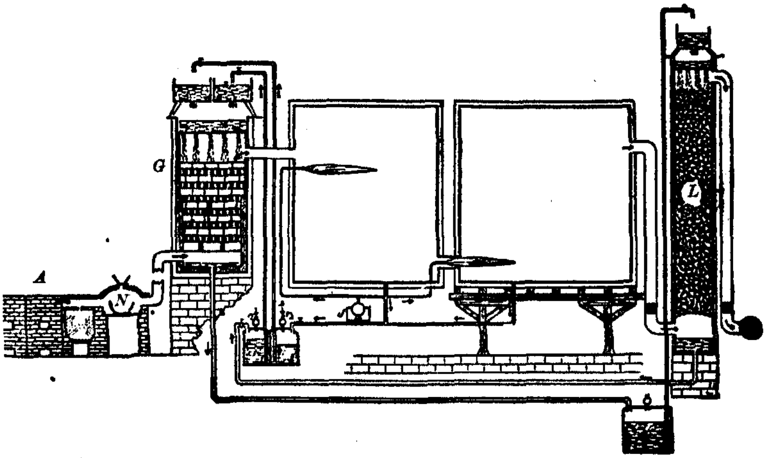


FIG. 84.

proportion of air, and have an opportunity to deposit oxides of iron and of arsenic and other materials which they transport mechanically. From this flue they enter the Glover tower *G*, in which they acquire the oxides of nitrogen. Having secured all the necessary constituents, excepting water, and having been reduced very considerably in temperature, the gases next enter the first of the lead chambers. These are large structures, from three to five in number, constructed completely of sheet lead. They vary in size, measuring as much as 100 × 40 × 40 feet, and sometimes having a total capacity of 150,000 to 200,000 cubic feet. As the gases drift through these chambers they

are thoroughly mixed, and an amount of water considerably in excess of that actually required, is injected in the form of steam at various points. The temperature in the first chamber is maintained at 50° to 65°, while in the last chamber it is about 15° above that of the outside air. The acid, along with the excess of water, condenses and collects upon the floor of the chamber, while the unused gases, consisting chiefly of nitrous anhydride and a very large amount of nitrogen, derived from the air originally admitted, find an exit into the Gay-Lussac tower *L*.

This is a tower about fifty feet in height, filled with tiles, over which concentrated sulphuric acid continually trickles from a reservoir at the top. The object of this tower is to catch the nitrous anhydride and enable it to be reëmployed in the process. This is accomplished by a reversal of action (2) above. The acid which accumulates in the vessel at the bottom of this tower contains the nitrosylsulphuric acid, and by means of compressed air is forced through a pipe up to a vessel at the top of the Glover tower *G*. When this "nitrous vitriol" is mixed with dilute sulphuric acid from a neighboring vessel, by allowing both to flow down into the tower, the nitrous anhydride is once more set free by the interaction of the water in the dilute acid (action (2)). The Glover tower is filled with broken quartz or tiles, and the heated gases from the furnace acquire in it their supply of nitrous anhydride. Their high temperature causes a considerable concentration of the diluted sulphuric acid as it trickles downward. The acid, after traversing this tower, is sufficiently strong to be used once more for the absorption of nitrous anhydride. To replace the nitrous anhydride inevitably lost by reduction to nitrous oxide and otherwise, fresh nitric acid is furnished by small open vessels *N*, containing sodium nitrate and sulphuric acid, placed in the flues of the pyrite-burners. About 4 kg. of the nitrate are consumed for every 100 kg. of sulphur.

The immense size of the chambers is necessitated by the fact that the chemical action, although much quicker than the direct oxidation of sulphurous acid, is after all rather slow. The presence of the large amount of atmospheric nitrogen, which diminishes the concentration of all the interacting substances, partly accounts for this slowness. The acid which accumulates upon the floors contains but 60 to 70 per cent of sulphuric acid, and has a specific gravity of 1.5–1.62. The excess of water is used to facilitate the second action. It is required also in order that the acid upon the floor may not afterwards absorb and

retain the nitrous anhydride, for this substance combines with an acid containing more than 70 per cent of hydrogen sulphate.

This crude sulphuric acid is applicable directly in some chemical manufactures, such as the preparation of superphosphates (*q.v.*). In most cases, however, a more concentrated sulphuric acid is required. The concentration is effected in the first place by evaporation in pans lined with lead, which are frequently placed over the pyrite-burners in order to economize fuel. The evaporation in lead is carried on until a specific gravity 1.7, corresponding to 77 per cent concentration, is reached. Up to this point the sulphate of lead formed by the action of the sulphuric acid produces a crust which protects the metal from further action. The insoluble sulphate of lead, however, becomes more soluble in sulphuric acid the more concentrated it is, and the higher, therefore, its boiling-point. For some applications of the acid, concentration beyond this point is not needed. When a stronger acid is required, the water is usually driven out by heating the sulphuric acid in vessels of glass or platinum. Commercial sulphuric acid, *oil of vitriol*, has a specific gravity 1.83–1.84, and contains about 93.5 per cent of sulphuric acid.

In modern sulphuric acid plants, the concentration beyond the specific gravity 1.77 is frequently carried out in vessels of cast iron, as that metal is attacked to an appreciable extent only by acids of lower specific gravity.

Physical Properties. — Pure hydrogen sulphate has a sp. gr. 1.85 at 15°. When cooled, it crystallizes (m.-p. 10°). At 150°–180° the acid begins to fume, giving off sulphur trioxide. At 330° it boils. The 100 per cent acid gives off sulphur trioxide, and the dilute acid water, until a mixture of constant composition (98.33 per cent) and constant b.-p. 330° is formed. This distils with unchanged composition (*cf.* p. 182). The vapor, however, contains 34 per cent of the material in the form of water and sulphur trioxide, which reunite when cooled.

When hydrogen sulphate is mixed with water a considerable evolution of heat takes place. This heat receives progressively diminishing increments as more water is added, until a very great dilution has been reached. The total is 19,400 cal. This heat of solution has not been accounted for quantitatively (*cf.* p. 165), but a part of it is due to the heat given out in connection with the ionization of the hydrogen sulphate. The solution is thus much more stable (*i.e.*, it contains much less energy)

than the pure substance, and hence the latter absorbs water greedily. Many substances containing hydrogen and oxygen are deprived of equivalent amounts of these elements by sulphuric acid, just as they are by sulphur trioxide (p. 381). The same tendency is enlisted to promote chemical actions in which water is formed, particularly in connection with the manufacture of nitroglycerine (*q.v.*), gun-cotton (*q.v.*), and esters (*q.v.*).

Impurities. — Commercial sulphuric acid is frequently brown in color on account of the presence of fragments of straw which have become charred and finally completely disintegrated. It contains also lead sulphate, which appears as a precipitate when the acid is diluted, as well as arsenic trioxide and oxides of nitrogen in combination, and many other foreign substances in small quantities. The pure sulphuric acid employed in chemical laboratories has received special treatment for the removal of these ingredients.

Chemical Properties of Hydrogen Sulphate. — The compound is not exceedingly stable, for dissociation into water and sulphur trioxide begins far below the boiling-point (*cf.* p. 387), and is practically complete at 416°, as is shown by the density of the gas. When raised suddenly to a red heat it is broken up completely into water, sulphur dioxide, and oxygen.

When mixed with a small quantity of water and cooled strongly it gives a crystalline monohydrate H_2SO_4, H_2O, which melts and is resolved into its constituents at 8°. Possibly this should be regarded as a different sulphuric acid, H_4SO_6 (*cf.* p. 278).

When sulphur trioxide is dissolved in hydrogen sulphate, **disulphuric acid** $H_2S_2O_7$, a solid compound, is obtained. Hydrogen sulphate containing 80 per cent of disulphuric acid is known as "oleum," and is employed in chemical industries. The old "fuming," or "Nordhausen" sulphuric acid contained 10–20 per cent of extra sulphur trioxide. The salts of disulphuric acid may be made by strongly heating the acid sulphates, for example:

$$2NaHSO_4 \rightleftarrows Na_2S_2O_7 + H_2O \uparrow.$$

In view of this mode of preparation by the aid of heat, they are frequently known as **pyrosulphates** (Gk. πῦρ, fire). When they are dissolved in water, the acid sulphates are reproduced.

On account of the large quantity of oxygen which hydrogen sul-

phate contains, and its instability when heated, it behaves as an oxidizing agent. This property has already been illustrated in connection with the action of the acid upon carbon and sulphur (p. 379) and upon copper (p. 379), hydrogen sulphide (p. 374), zinc (p. 96), and, particularly, hydrogen iodide (p. 237) and hydrogen bromide (p. 231). The sulphuric acid is in consequence reduced to sulphur dioxide, and even to free sulphur or hydrogen sulphide. The metals, from the most active down to silver (p. 362), are capable of reducing it. Gold and platinum alone are not attacked, and hence their use in making sulphuric acid stills. Free hydrogen itself is oxidized to water when passed into hydrogen sulphate at 160°:

$$SO_2(OH)_2 + H_2 \rightarrow SO_2 + 2H_2O.$$

With salts which it does not oxidize, hydrogen sulphate reacts by double decomposition and sets free the corresponding acid. The actions are always reversible ones; but where the new acid is volatile, as in the case of hydrogen chloride (p. 180), we are furnished with one of the cheapest means of preparing acids.

Since hydrogen sulphate is dibasic, that is, since it has two units of hydrogen which may be replaced by a metal, it forms both acid and neutral salts.

Chemical Properties of Aqueous Hydrogen Sulphate. — The solution of sulphuric acid is a mixture whose components are: undissociated molecules H_2SO_4, hydrion $H^{\cdot}$, hydrosulphanion HSO_4', and sulphanion SO_4''. The chemical properties shown by the solution are those of one or other of these components, according to circumstances.

Except in concentrated solutions (normal or stronger) the oxidizing effects of the undissociated, molecular substance are not encountered. The temperature of the diluted acid, even when boiling, is not high enough for the purpose. In fairly strong solutions hydrosulphanion is plentiful and shows itself in the results of electrolysis (see p. 397).

The presence of hydrion is shown by all its usual properties (p. 345). In the following table the proportion of the whole of the hydrogen existing in the form of hydrion (column five) and its concentration (column six), taking a normal solution of hydrion containing 1 g. per liter as standard, are shown (*cf.* pp. 149 and 329). The first three columns give the concentration of the sulphuric acid as a whole, in terms (first column) of the volume of liquid containing one equivalent ($\frac{1}{2}H_2SO_4 = 49$ g.), in terms (second column) of a normal solution as

standard, and by per cent (third column), respectively. The fourth column shows the conductivity (p. 328).

v	H_2SO_4	PER CENT H_2SO_4.	λ_v	λ_v/λ_∞	$H^{\cdot}$
0.1	10 N	38.00	70	0.18	1.8 N
1	N	4.79	198	0.51	0.51 N
10	0.1 N	0.48	225	0.58	0.058 N
100	0.01 N	0.05	308	0.79	0.0079 N
1000	0.001 N	0.005	361	0.93	0.00093 N
∞	0	0.00	388	1.00	0.00

Column 5 thus states that in a normal solution 51 per cent, and in a centi-normal solution 79 per cent of the hydrogen is ionic.

Sulphanion SO_4'' unites with all positive ions. The product, when insoluble, appears as a precipitate. The introduction of barium ions, for example, by adding a solution of barium nitrate or chloride, is employed as a means of recognizing the presence of sulphanion:

$$Ba^{\cdot\cdot} + SO_4'' \rightleftarrows BaSO_4\downarrow.$$

Naturally this test is given by solutions of all soluble acid and normal sulphates. Since there are other barium salts which are insoluble in water, but no common ones which are not decomposed by acids, dilute nitric acid is first added to the solution supposed to contain the sulphanion. The other ions, if present, then give no precipitate with barion.

Sulphates. — The **acid sulphates**, known also as *bisulphates*, may be produced either by semi-neutralization of sulphuric acid with a base, followed by evaporation: $NaOH + H_2SO_4 \leftrightarrows H_2O + NaHSO_4$, or by actions in which another acid is displaced, as in making hydrogen chloride (p. 179).

The neutral (or normal) sulphates are obtained by complete neutralization and evaporation, or by the second of the above methods when a sufficient amount of the salt and a higher temperature are used:

$$NaCl + NaHSO_4 \rightleftarrows Na_2SO_4 + HCl\uparrow.$$

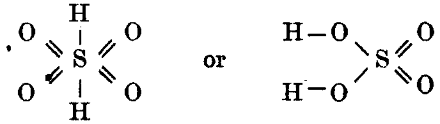
They are often made also by precipitation, by oxidation of a sulphide at a high temperature, $PbS + 2O_2 \rightarrow PbSO_4$, or by addition of sulphur trioxide to the oxide of a metal (p. 381).

Acid sulphates, when heated, yield pyrosulphates (p. 388). Normal sulphates of the heavy metals decompose at a white heat, giving off

sulphur trioxide (p. 380). The sulphates of potassium, sodium, and others of the more active metals, however, are not affected by heating.

When a sulphate, or indeed any salt of a sulphur acid, is heated strongly with carbon, the oxygen is removed and a sulphide remains: $Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$. Upon this is founded a general **test** for the presence of sulphur in any substance. The material to be tested is mixed with sodium carbonate. A small amount of the mixture is placed on the end of a match, which has been charred and rendered partially incombustible by previous application of sodium carbonate. When the end of the match is now held in the reducing part of the Bunsen flame, the compound of sulphur, if it contains oxygen, is reduced to the form of sulphide. This, by interaction with the carbonate, gives sodium sulphide, Na_2S. When the product of the reduction is placed upon a silver coin and moistened, the sodium sulphide, if present, produces a black stain of silver sulphide. This is known as the *hepar test*, hepar being an old name for a sulphide.

Constitution of Hydrogen Sulphate. — The formula which we assign to sulphur trioxide is $O{=}S\begin{matrix}\nearrow O\\ \searrow O\end{matrix}$. It is in general our desire to use the smallest possible valence, but here no reduction can be effected below the value 6 for the sulphur, unless we join the oxygen units to one another, as in the formula $O{=}S\begin{matrix}/O\\ \quad|\\ \backslash O\end{matrix}$. This, however, would suggest a relationship to hydrogen peroxide, $\begin{matrix}O-H\\ |\\ O-H\end{matrix}$, which is not confirmed, for hydrogen peroxide cannot be made from sulphuric acid. Assuming, therefore, the above formula for sulphur trioxide, the addition of the elements of water to it in the simplest fashion results in the structures:

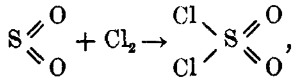


The second of these two modes of disposing of the water is the one which, in parallel cases, is usually most feasible. Hardly any alternative to it is possible, for example, in representing the action in which quicklime is slaked (p. 119):

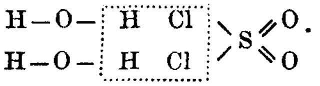
$$H_2O + O{=}Ca \rightarrow \begin{matrix}H-O\searrow\\ H-O\nearrow\end{matrix}Ca$$

This represents the change with little derangement of the original structure and without alteration in the valence, while the first unwarrantably increases the valence to ten. There are other objections to the first formula. In it the hydrogen is supposed to unite more immediately with the sulphur, whereas, when the free elements are concerned, hydrogen actually combines more readily with oxygen, and forms a more stable compound with it than with sulphur. Again, compounds like hydrogen sulphide, H—S—H, in which the hydrogen is undoubtedly united to sulphur, are but slightly ionized, and are feeble acids, while hydrogen sulphate is highly ionized.

Another fact is more satisfactorily accounted for by the second formula. The addition of chlorine to sulphur dioxide must be shown thus:



for chlorine has a much greater tendency to unite with sulphur than with oxygen. When the product, sulphuryl chloride, is brought in contact with water, sulphuric acid and hydrogen chloride are produced. Since water has the formula H—O—H, and two molecules of water are used, this action is most simply accounted for, with the minimum of disturbance in both molecules, by imagining the operation to take place as follows:



The hydrogen chloride is eliminated, and the other units of hydrogen, originally without doubt attached to oxygen in the water, may be presumed to be still connected with that oxygen when they enter the molecule of hydrogen sulphate.

This illustration shows the sort of reasoning, based upon the chemical properties and the modes of formation of a substance, which lead us to the devising of an appropriate graphic or structural formula (*cf.* p. 224). The latter is not supposed in any sense to represent the actual physical structure of the molecule, but simply to be a diagrammatic representation of the chemical relations of the constituents and of the chemical behavior of the whole. Formulæ of this kind are in continual use in the study of the compounds of carbon, but are seldom required outside of that region.

Uses of Sulphuric Acid. — Sulphuric acid is employed in almost all chemical industries, and in some of them (*q.v.*) the quantities required are very great. It is used, for example, in the first stage of the Le Blanc process for the manufacture of soda, in the refining of petroleum, in the manufacture of fertilizers, in the preparation of nitroglycerine and gun-cotton, and in the production of coal-tar dyes.

Other Acids of Sulphur.

Hyposulphurous Acid. — The zinc salt of this acid crystallizes out when zinc acts upon a solution of sulphur dioxide in absolute alcohol:

$$Zn + 2SO_2 \rightarrow ZnS_2O_4.$$

Whether the acid is monobasic or dibasic, and its formula HSO_2 or $H_2S_2O_4$, is still uncertain.

Commercially a solution containing the sodium salt is made by the interaction of zinc with a solution of sodium bisulphite charged with excess of sulphur dioxide:

$$2NaHSO_3 + SO_2 + Zn \rightarrow Na_2S_2O_4 + ZnSO_3 + H_2O.$$

The acid and its salts are very rapidly oxidized by the air, the former giving sulphurous acid and then sulphuric acid. The above solution of sodium hyposulphite is used in indigo dyeing, on account of its high reducing power. Indigo, which is insoluble, is reduced by the salt to indigo-white which passes into solution. When cloth saturated with the mixture, however, is exposed to the air, the salt is rapidly oxidized, the indigo-white likewise undergoes oxidation, and blue, insoluble indigo is formed once more (see Dyeing).

Sulphurous Acid. — This term is applied to the solution of sulphur dioxide in water. A portion of the sulphur dioxide remains dissolved physically, while another portion is in combination with the water, forming sulphurous acid. This in turn is ionized, and chiefly, after the manner of the weaker dibasic acids, into two ions, $H^{\cdot}$ and HSO_3'. A little SO_3'' is formed from the latter. There are thus in such a solution four mutually dependent equilibria:

$$SO_2\,(gas) \rightleftarrows SO_2\,(diss'd) + H_2O \rightleftarrows H_2SO_3 \rightleftarrows H^{\cdot} + HSO_3' \rightleftarrows H^{\cdot} + SO_3''.$$

When the solution is heated, uncombined sulphur dioxide is disengaged as a gas. The equilibria being thus disturbed, the ions of the acid

unite, the acid molecules decompose, and soon all the above actions are completely reversed and the whole of the gas passes off. Conversely, when a base furnishing hydroxyl ions is added to the solution of the acid, the hydrogen ions disappear, forming water, and the above actions all proceed in a forward direction until, with a half-equivalent of the base, the whole of the material has been converted into the form HSO_3', in association, of course, with the positive ions of the base. With a full equivalent, neutralization follows and SO_3'' is the product.

Properties of Sulphurous Acid. — The acid is so unstable that it cannot be obtained at ordinary temperatures excepting in solution in water. Chemically it is a comparatively weak acid. As a reducing agent, it is slowly oxidized by free oxygen, and rapidly by oxidizing agents, turning into sulphuric acid. Thus, when free halogens are added to the solution, sulphuric acid and the hydrogen halide are formed:

$$H_2SO_3 + H_2O + I_2 \rightleftarrows H_2SO_4 + 2HI.$$

In the particular case of iodine this action takes place only in very dilute solution, since concentrated sulphuric acid decomposes hydrogen iodide (*cf.* p. 237) and the action is reversed. This interaction is used in chemical analysis as a means of estimating the quantity of sulphurous acid in a liquid (*cf.* p. 236).

Hydrogen peroxide, potassium permanganate, and other oxidizing agents convert the substance into sulphuric acid likewise. It should be noted that in these oxidations we have, not an addition of oxygen to SO_2, but to the SO_3'' or HSO_3' ion of the acid, whereby it passes into the SO_4'' ion of sulphuric acid. The ion is much more easily oxidized than is free sulphur dioxide itself.

Sulphurous acid has the power of uniting directly with many organic coloring matters and, since the products of this union are usually colorless, it is employed as a bleaching agent. It is especially useful with materials like silk, wool, and straw, which are likely to be destroyed by chlorine. Exposure to sunlight causes the dissociation of these colorless compounds, and so, with use, straw hats slowly recover their original color. As a disinfectant it acts by addition likewise.

As a dibasic acid, sulphurous acid forms normal salts like Na_2SO_3, and acid salts like $NaHSO_3$.

Illustration of the Effect of Concentration on Speed of Interaction. — The oxidation of sulphurous acid by iodic acid may be used to show the effect of concentration on the speed of an action

(p. 252). The iodic acid may most readily be made by dissolving potassium iodate and sulphuric acid together in water, in such quantities as would give a N/2 solution of each. When 1 c.c. of this N/2 iodic acid is added to 100 c.c. of filtered starch emulsion, and the whole is mixed with an equal volume of water containing 1 c.c. of N/2 sulphurous acid, the blue color produced by the liberated iodine appears suddenly after the lapse of a minute or more:

$$2HIO_3 + 5H_2SO_3 \rightarrow 5H_2SO_4 + H_2O + I_2.$$

With double the above quantities in the same amount of water, that is, with double concentrations, the speed of the action is greatly increased and the iodine becomes visible in less than half the time.

Sulphites. — The acid sulphites of the alkali metals (*i.e.*, of potassium and sodium) are acid in reaction, owing to the appreciable dissociation of the ion HSO_3'. The acid being a weak one, however, solutions of the normal salts, Na_2SO_3, etc., are alkaline towards litmus (p. 344). The sulphites are readily decomposed by acids giving free sulphurous acid, and the latter partly decomposes, yielding sulphur dioxide.

Calcium bisulphite solution, $Ca(HSO_3)_2$, is used to dissolve the lignin out of wood employed in the manufacture of paper. About 30 per cent of the wood is lignin. The rest is cellulose $(C_6H_{10}O_5)_x$, and constitutes the prepared pulp.

When heated, sulphites undergo decomposition. The sulphates, being the most stable of all the salts of sulphur acids, are formed when the salts of any of those acids are decomposed by heating. The nature of the particular salt determines what other products shall appear. Here, one molecule of the sulphite furnishes three atoms of oxygen, sufficient to oxidize three other molecules, and leaves one molecule of sodium sulphide behind:

$$4Na_2SO_3 \rightarrow Na_2S + 3Na_2SO_4.$$

The acid sulphites (bisulphites) first lose sulphurous acid, before changing in this way. Thus, sodium hydrogen sulphite begins by decomposing as follows:

$$2NaHSO_3 \rightarrow Na_2SO_3 + H_2SO_3 \text{ (or } H_2O + SO_2\text{)}.$$

The acid salts of volatile acids, when heated, all decompose in this way (*cf.* pp. 241, 388).

The sulphites are as readily oxidized as is the acid itself. They are

slowly converted, both in solution and in the solid form, by the influence of the oxygen of the air, into sulphates. It is interesting to note that the addition of sugar or glycerine to a solution of a sulphite reduces the speed of oxidation by free oxygen very markedly. These substances act as catalytic agents; and the present case shows that agents of this kind may not only increase the speed of actions, which is their usual function, but may also have a restraining influence.

Thiosulphuric Acid. — This acid is not known in the free condition, but its salts are in common use in the laboratory and commercially. The sodium salt, for example, is prepared by boiling a solution of sodium sulphite with free sulphur. The action is something like the addition of oxygen to sulphurous acid:

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3 \quad \text{or} \quad SO_3'' + S \rightarrow S_2O_3''.$$

The product, thiosulphate of sodium, is used in photography as a solvent for salts of silver, and is commonly known as *hyposulphite of soda.* Its solution in water forms the *fixing bath* of the photographer.

By the addition of acids to a solution of sodium thiosulphate, the thiosulphuric acid is set free, but the latter instantly decomposes:

$$Na_2S_2O_3 + 2HCl \rightleftarrows H_2S_2O_3 + 2NaCl,$$
$$H_2S_2O_3 \rightleftarrows H_2SO_3 + S\downarrow.$$

Even carbon dioxide from the air, giving carbonic acid (*q.v.*), produces this effect slowly in fixing solutions. The actions being reversible, preliminary addition of a sulphite to the solution helps to sustain the reverse action, in which sulphurous acid is a factor, and so preserves the solution. The delay in the appearance of the precipitate of sulphur in dilute solutions is due to the temporary existence of a supersaturated solution (*cf.* p. 160) of the free element.

Iodine acts upon sodium thiosulphate solution, giving sodium tetrathionate:

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6.$$

This action is used, by employment of a standard solution of sodium thiosulphate, for estimating quantities of free iodine in analysis. The disappearance of the color of the latter indicates that a sufficient amount of the salt has been employed. When chlorine is used, the oxidation is more complete. The products are sodium sulphate, sulphuric acid, and hydrochloric acid:

$$Na_2S_2O_3 + 5H_2O + 4Cl_2 \rightarrow Na_2SO_4 + H_2SO_4 + 8HCl.$$

In consequence of the very great amount of free chlorine which the sodium thiosulphate is thus able to transform, it is employed, as *antichlor*, for the purpose of removing chlorine from bleached fabrics.

Persulphuric Acid. — This, like the other acids just mentioned, is unstable, and can be kept only in very dilute solution. Its salts, however, are coming into use for commercial purposes and for "reducing" negatives in photography. When a discharge of electricity is passed through a mixture of sulphur trioxide and oxygen, drops of liquid are formed which appear to have the composition S_2O_7, and when dissolved in water give dilute persulphuric acid, $S_2O_7 + H_2O \rightarrow H_2S_2O_8$. More significant of its relations is its formation, to some extent, when concentrated sulphuric acid and a strong solution of hydrogen peroxide are mixed:

$$2H_2SO_4 + H_2O_2 \rightleftarrows H_2S_2O_8 + 2H_2O.$$

This action is reversible.* Under some circumstances, monopersulphuric acid is formed: $H_2SO_4 + H_2O_2 \rightleftarrows H_2SO_5 + H_2O$. Interesting in its way, also, is its production in the electrolysis of aqueous sulphuric acid:

$$2H\bar{S}O_4 + 2 \oplus \rightarrow H_2S_2O_8.$$

This action is most conspicuous in rather concentrated solutions in which hydrosulphanion is plentiful (*cf.* p. 389) and when a small anode, resulting in severe crowding of the HSO_4 radicals as they are liberated, is employed. The salts are prepared by electrolyzing sodium hydrogen sulphate $NaHSO_4$ in concentrated solution. The persulphuric acid, formed by the union of the negative ions in pairs, undergoes double decomposition with the excess of sodium bisulphate, and the less soluble sodium persulphate crystallizes out. The other salts are made by double decomposition from this one.

* This action and the next are not easily classifiable under any of the ten kinds formerly discussed (p. 187). They consist in the union of H and OH to form water:

$$HSO_4 \vdots\ H + HO\ \vdots\ OH + H\ \vdots\ SO_4H \rightarrow 2H_2O + (SO_4H)_2.$$

Neutralizations (p. 351) they are not, because the interacting substances are both acids. Just as the loss of water from one acid gives an anhydride, so here, the loss of water between two acids gives a mixed **anhydride** (see Chlorosulphuric acid, below).

The persulphates decompose readily when heated, yielding pyrosulphates and oxygen:

$$2K_2S_2O_8 \rightarrow 2K_2S_2O_7 + O_2.$$

The solution of the acid is an active oxidizing agent:

$$H_2S_2O_8 + H_2O \rightarrow 2H_2SO_4 (+ O).$$

Polythionic Acids. — Di-, tri-, tetra-, and pentathionic acid (p. 381) are all formed simultaneously when sulphur dioxide and hydrogen sulphide gases are passed alternately into water, although the gases themselves (p. 373) interact to produce simply free sulphur and water:

$$H_2S + 3SO_2 \rightarrow H_2S_4O_6,$$
$$2H_2S + 6SO_2 \rightarrow H_2S_3O_6 + H_2S_5O_6,$$
$$3H_2S + 9SO_2 \rightarrow H_2S_2O_6 + 2H_2S_5O_6.$$

Most of these acids and their salts are of minor interest and need not be discussed.

The production of sodium tetrathionate by the action of iodine upon sodium thiosulphate has already been mentioned.

When manganese dioxide is treated with sulphurous acid, it interacts very rapidly and a solution of manganous dithionate is obtained:

$$MnO_2 + 2H_2SO_3 \rightarrow MnS_2O_6 + 2H_2O.$$

The salts of these acids are in many cases fairly stable, but the acids themselves decompose readily when set free.

Compounds of Sulphur and Chlorine.

Sulphur Monochloride. — When chlorine gas is passed over heated sulphur it is absorbed, and a dark reddish-yellow liquid, boiling at 138°, is obtained. The molecular weight of this substance, as shown by the density of its vapor, indicates that it possesses the formula S_2Cl_2. When thrown into water it is rapidly hydrolyzed, producing sulphur dioxide and free sulphur:

$$2S_2Cl_2 + 2H_2O \rightarrow SO_2 + 4HCl + 3S.$$

Sulphur itself dissolves very freely in the monochloride, and the solution is employed in vulcanizing rubber.

By surrounding sulphur monochloride with a freezing mixture, and treating it with excess of chlorine, a liquid **tetrachloride** SCl_4 is formed. This gives up chlorine, and turns into the monochloride again, when allowed to become warm.

Thionyl Chloride. — By the action of sulphur dioxide gas upon phosphorus pentachloride, part of the oxygen in the former is replaced by chlorine:

$$SO_2 + PCl_5 \rightarrow SOCl_2 + POCl_3.$$

The products are thionyl chloride and phosphorus oxychloride. The former is a colorless liquid, boiling at 78°, and is separated from the latter (b.-p. 107°) by fractional distillation (see Petroleum). It is decomposed immediately on contact with water:

$$SOCl_2 + H_2O \rightarrow SO_2 + 2HCl.$$

Sulphuryl Chloride. — Sulphur dioxide and chlorine gases unite when exposed to direct sunlight to form a liquid known as sulphuryl chloride SO_2Cl_2. When camphor is introduced into the vessel the union takes place much more rapidly, owing to some catalytic effect of this substance. The compound is a colorless liquid, boiling at 69°. With water it gives sulphuric acid and hydrogen chloride (p. 392). When a strictly limited amount of water is supplied, a partial action of the same nature occurs, and the product is known as **chlorosulphuric acid**:

$$SO_2Cl_2 + H_2O \rightarrow SO_2\left\langle{Cl \atop OH}\right. + HCl.$$

This intermediate compound may be formed also by the addition of hydrogen chloride to sulphur trioxide.

Exercises. — 1. What ground is there for assigning the formula SO_2 instead of S_2O_4 to sulphur dioxide (p. 193)?

2. Explain why nitric acid is completely displaced by the action of sulphuric acid on sodium nitrate (p. 384).

3. How many times, on an average, does a molecule of nitrous anhydride go through the cycle of changes by which sulphuric acid is produced before it is eliminated in some other form (p. 386)?

4. Make a list of, and classify, the various applications of sulphuric acid to the liberation of other acids.

5. Formulate the behavior of the hydrosulphanion (p. 389) when a solution of barium chloride is added to a rather concentrated solution of sulphuric acid.

6. Can you give any reasons for preferring to regard $KHSO_4$, and substances like it, as acid salts rather than double salts of the form K_2SO_4, H_2SO_4 (p. 358)?

7. From a consideration of the physical conditions, how can you account for the fact that hyposulphurous acid is oxidized by free oxygen first to sulphurous acid and then to sulphuric acid (p. 393), while moist free sulphur, even with oxidizing agents, gives sulphuric acid directly (p. 371)?

8. Why were not disulphuric acid and monopersulphuric acid placed in the list on p. 381 (*cf.* p. 278)?

9. Write in ionic form the equation for the interaction of sodium thiosulphate and iodine in aqueous solution.

10. Restate the import of the following sentence in such a way as to avoid the use of the hypothesis of ions: Liquefied sulphur dioxide "ionizes substances dissolved in it as well as does water" (p. 379).

CHAPTER XXIII

SELENIUM AND TELLURIUM: THE PERIODIC SYSTEM

Along with sulphur, chemists group two other elements, selenium (Se, at. wt. 79.2) and tellurium (Te, at. wt. 127.6). If the nature of the chief compounds of sulphur is kept in mind, the close analogy between the nature and chemical behavior of the three elements and their corresponding compounds will be noticed at once (see Chemical relations of the sulphur family, below).

Selenium.

Occurrence and Properties of the Element. — Selenium (Gk. σελήνη, the moon) occurs free in some specimens of native sulphur, and in combination often takes the place of a small part of the sulphur in pyrite (FeS_2). It is found free in the dust-flues of the pyrite-burners of sulphuric acid works. The familiar forms are, the red precipitated variety, which is amorphous and soluble in carbon disulphide, and the lead-gray, semi-metallic variety, obtained by slow cooling of melted selenium, which is insoluble, and melts at 217°. In the latter form it has some capacity for conducting electricity, which is increased by exposure to light in proportion to the intensity of the illumination. It boils at 680°, and at high temperatures has a vapor density corresponding to the formula Se_2.

The element unites directly with many metals, burns in oxygen to form selenium dioxide, and unites vigorously with chlorine.

Hydrogen Selenide. — Ferrous selenide, made by heating iron filings with selenium, when treated with concentrated hydrochloric acid gives hydrogen selenide:

$$FeSe + 2HCl \rightleftarrows H_2Se\uparrow + FeCl_2.$$

The compound is a poisonous gas, which possesses an odor recalling rotten horse-radish, and is soluble in water. The solution is faintly acid in reaction, and deposits selenium when exposed to the action of

the air (*cf.* p. 373). Other selenides, which, with the exception of those of potassium and sodium, are insoluble in water, may be precipitated by leading the gas into solutions of soluble salts of appropriate metals (*cf.* p. 375).

Selenium Dioxide and Selenious Acid. — The dioxide (SeO_2) is a solid body formed by burning selenium or evaporating a solution of selenious acid H_2SeO_3. The latter may be made directly by oxidizing selenium with boiling nitric acid or *aqua regia* (*q.v.*). Unlike sulphur (p. 371), the element gives little of the higher acid H_2SeO_4 by this treatment. In aqueous solution the acid is easily reduced to selenium. In fact, sulphurous acid can be oxidized by it:

$$H_2SeO_3 + 2H_2SO_3 \rightarrow 2H_2SO_4 + H_2O + Se.$$

Selenic Acid. — No trioxide is known. Selenic acid (H_2SeO_4) is made by using the most powerful oxidizing agents with an aqueous solution of selenious acid. It can be isolated as a white solid. It is itself a powerful oxidizing agent, and, even in dilute solution, liberates chlorine from hydrochloric acid:

$$H_2SeO_4 + 2HCl \rightarrow H_2SeO_3 + H_2O + Cl_2.$$

Sulphuric acid (*cf.* p. 389), on the other hand, is an oxidizing agent only in somewhat concentrated form, and even then it can oxidize hydrobromic acid (p. 231), but not hydrochloric acid.

Chlorides of Selenium. — The chlorides are formed by direct union of the elements. The tetrachloride, a yellow crystalline substance, is formed when the monochloride is heated: $2Se_2Cl_2 \rightarrow 3Se + SeCl_4$, the behavior in the case of sulphur chlorides being just the inverse of this (p. 399).

Tellurium.

Tellurium (Lat. *tellus*, the earth) occurs in sylvanite in combination with gold and silver. It is a white, metallic, crystalline substance, melting at 452°. When formed by precipitation it is a black powder. It conducts electricity to some extent. The vapor density corresponds to the formula Te_2.

The free element unites with metals directly, and burns in air to form the dioxide.

Hydrogen telluride (H_2Te) is made by the action of acids on metallic tellurides, and its aqueous solution is rapidly oxidized by air with precipitation of tellurium. The tellurides of the alkali metals are soluble in water, the others are insoluble.

Tellurious acid (H_2TeO_3) is formed by oxidizing the element with nitric acid, and is a crystalline solid, little soluble in water. It is a feeble acid, of which many salts have been made. It is also somewhat basic, a sulphate ($2TeO_2, SO_3$) and a nitrate ($Te_2O_3(OH)NO_3$) being known. In this respect it differs markedly from sulphurous acid.

Telluric acid is made by oxidizing tellurious acid in aqueous solution with chromic acid (p. 374). It is difficultly soluble in water. It does not affect indicators, and is therefore actually more feebly acidic than is hydrogen sulphide. It is obtained as a solid having the composition H_6TeO_6 (or $3H_2O, TeO_3$) on evaporating the solution. When heated, this body loses water, some of the trioxide (TeO_3) being formed. The last is a yellow solid, which shows no tendency to recombine with water, in this respect resembling silica (*q.v.*). Tellurates of the alkali metals may be made by heating the tellurites with potassium or sodium nitrate: $K_2TeO_3 + KNO_3 \rightarrow K_2TeO_4 + KNO_2$.

Tellurium forms two very stable chlorides, $TeCl_2$ and $TeCl_4$, which are decomposed by water. The second, however, exists in solution with excess of hydrogen chloride: $TeCl_4 + 3H_2O \rightleftarrows H_2TeO_3 + 4HCl$, showing the tellurious acid to be basic in properties and the element tellurium to be, to a certain degree, a metal (see Chap. xxxii).

The Chemical Relations of the Sulphur Family.—It will be seen that sulphur, selenium, and tellurium are bivalent elements when combined with hydrogen or metals. In combination with oxygen they form unsaturated compounds of the form $X^{IV}O_2$, while their highest valence is found in SO_3, TeO_3, and H_2SeO_4, where they must be sexivalent. The general behavior of corresponding compounds is very similar. At the same time, there is in all cases a progressive change as we proceed from sulphur through selenium to tellurium. The elementary substances themselves, for example, become more like metals, physically, and they show higher and higher melting-points. The affinity for hydrogen decreases, as is shown by the increasing ease with which the compounds H_2X are oxidized in air. The affinity for oxygen likewise decreases, for the elements become increasingly difficult to raise to the highest state of oxidation. On the other hand,

the tendency to form higher chlorides becomes greater. We note also that the compounds H_2XO_4 become less and less active as acids, and a basic tendency begins to assert itself.

THE PERIODIC SYSTEM.

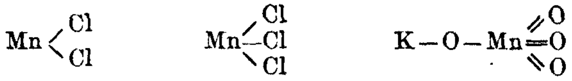
Classification, or the arrangement of facts on the basis of likeness, is part of the method of science. In chemistry the multitude of facts is not less than in other sciences, and the necessity of arrangement equally urgent. It is needed to make possible the systematic description of the ascertained facts, and to furnish a guide in investigation, by suggesting stochastic hypotheses, and so pointing out directions in which new facts of interest may be found. Thus, we have treated the halogens as a group; and chemists, knowing how hypochlorous acid (HClO) and perchloric acid ($HClO_4$), and their salts, are made, have been led to attempt to obtain related substances, like HIO and $HBrO_4$ and their salts, by methods suggested by analogy.

At first sight, the most definite method of classification would appear to be the grouping of elements of like valence. But this brings together sodium and chlorine — an element whose hydrogen compound is unstable and without markedly characteristic properties, and whose hydroxyl compound is an active base, with an element whose hydrogen compound is an active acid and whose hydroxyl compound is, in a feeble degree, an acid also. This method homologates similar and contrasting elements indiscriminately.

Metallic and Non-Metallic Elements. — Thus far we have found the division into metallic and non-metallic elements very serviceable for classification in terms of chemical relations (p. 177). This distinction we shall continue to employ. **The metals, or positive elements** (p. 119), (1) form positive ions containing no other element (*cf.* p. 337). Thus the metals give sulphates, nitrates, carbonates, and other salts, which furnish a metallic ion together with the ions SO_4'', NO_3', and CO_3''. (2) Their hydroxides, KOH, $Ca(OH)_2$, etc., give the same metallic ion, and the rest of the molecule forms hydroxidion. That is to say, their hydroxides are bases and their oxides are basic. They often enter with other elements into the composition of a negative ion, as is the case with manganese in $K.MnO_4$, with chromium in $K_2.Cr_2O_7$, and with silver in $K.Ag(CN)_2$.* But the most definitely metallic elements form with

* The mode of division into ions is shown by the position of the period in the formula.

oxygen such a negative ion only while exhibiting a ***different valence*** from that which they possess when acting as positive elements. Thus, manganese when a positive element has the valences two and three, MnO and Mn_2O_3, $Mn.Cl_2$ and $Mn.Cl_3$, $Mn.SO_4$ and $Mn_2.(SO_4)_3$, etc., while in permanganates we have potentially the oxide Mn_2O_7, (K_2O, $Mn_2O_7 = 2KMnO_4$), in which it is heptavalent. The graphic formulæ express the difference in valence:



Manganese forms no heptachloride or heptanitrate (corresponding to the heptoxide) in which manganese alone would form a heptavalent positive ion on the one hand, and no compound in which bivalent or trivalent manganese with oxygen form the negative ion, on the other. Chromium (*q.v.*) is bivalent or trivalent when a metal, and sexivalent when acting as a non-metal. The various hydroxides of these elements are bases or acids in accordance with this distinction. If we knew only the compounds in which manganese and chromium are heptavalent and sexivalent, respectively, we should regard them as non-metallic elements pure and simple, the metallic appearance of the free elements to the contrary notwithstanding.

The non-metals or negative elements, (1) are found chiefly in negative ions. They form no nitrates, sulphates, carbonates, etc., for they could not do so without themselves constituting the positive ion. We have no such salts of oxygen, sulphur, carbon, or phosphorus, for example. (2) Their hydroxides, like ClO_2OH, $P(OH)_3$, $SO_2(OH)_2$, furnish no hydroxyl ions, as this would involve the same consequence. These hydroxides are divided by dissociation, in fact, so that the non-metal forms part of a compound negative radical, and the other ion is hydrion, $ClO_3.H$, $PO_3H.H_2$, $SO_4.H_2$. (3) Their halogen compounds, like PCl_3 (p. 181) and S_2Cl_2 (p. 398), are completely hydrolyzed by water, and the actions are not, in general, reversible. The halides of the typical metals are not hydrolyzed (see Chap. xxxii).

The distinction is not perfectly sharp, however. Thus, zinc (*q.v.*) gives, both salts like the sulphate, $Zn.SO_4$, and chloride, $Zn.Cl_2$, and compounds like sodium zincate (p. 99), $ZnO_2.Na_2$, showing the same valence in both classes:

Its hydroxide ionizes in two ways, $Zn.(OH)_2$ and $ZnO_2.H_2$. Similarly tellurious acid, H_2TeO_3, acts both as acid and base (p. 403). We shall find this double behavior conspicuous in the compounds of arsenic and antimony. In spite of the partial merging of the two classes of elements, however, the general distinction is worth preserving (see Chap. xxxii).

Classification by Atomic Weights. — A closer discrimination than that furnished by these two categories is required, however, and a study of the order into which the elements fall when arranged according to their atomic weights has provided this.

The first indication of a significant relation between the atomic weights and the properties of the elements was given by a fact noted by Döbereiner (1829). He drew attention to the existence of closely similar elements in sets of three (**triads**), where the central element was intermediate in properties between the two others, and the atomic weight of the central element was almost the exact arithmetical mean of the weights of the other two. The three following triads illustrate this relation:

Chlorine . . .	35.45	Sulphur . . .	32.06	Calcium	40.1
Bromine . . .	79.96	Selenium . . .	79.2	Strontium . . .	87.6
Iodine . . .	126.97	Tellurium . . .	127.6	Barium	137.4
Mean of Cl and I,	81.1	Mean of S and Te,	79.8	Mean of Ca and Ba,	88.7

Newlands (1863–4) called attention to the existence of a surprising regularity when the elements were placed in the order of ascending atomic weight. Omitting hydrogen (1) the first seven are: lithium (7), glucinum (9), boron (11), carbon (12), nitrogen (14), oxygen (16), fluorine (19). These are all of totally different classes, and include first a metal forming a strongly basic hydroxide, then a metal of the less active sort, then five non-metals of increasingly negative character, the last being the most active non-metal known. The next element after fluorine (19) is sodium (23), which brings us back sharply to the elements that form strongly basic hydroxides. Omitting none, the next seven elements are: sodium (23), magnesium (24.4), aluminium (27), silicon (28.4), phosphorus (31), sulphur (32), chlorine (35.5).

In this series there are three metals of diminishing positiveness, followed by four non-metals of increasing negative activity, the last being a halogen very like fluorine. On account of the fact that each element resembles most closely the eighth element beyond or before it in the list, the relation was called the **law of octaves**. After chlorine

the octaves become less easy to trace. Potassium (39) follows chlorine and corresponds satisfactorily to sodium, but it is not until seventeen successive elements have been set down that we reach one closely resembling chlorine, namely, bromine.

That this periodicity in chemical nature is more than a coincidence is shown by the fact that the valence and even the physical properties, such as the specific gravity, show a similar fluctuation in each series, and recurrence in the following one. In the first two series the compounds with other elements are of the types:

$$LiCl,\ GlCl_2,\ BCl_3,\ CCl_4,\ \begin{cases} N_2O_5 \\ NH_3,\ OH_2,\ FH. \end{cases}$$

$$NaCl,\ MgCl_2,\ AlCl_3,\ SiCl_4,\ \begin{cases} P_2O_5,\ SO_3,\ Cl_2O_7 \\ PH_3,\ SH_2,\ ClH. \end{cases}$$

Thus the valence towards chlorine or hydrogen ascends to four and then reverts to one in each octave. The highest valence, shown in oxygen compounds, ascends from lithium to nitrogen with values one to five, and then fails because compounds are lacking. In the second octave, however, it goes up continuously from one to seven.

Again, the specific gravities of the elements in the second series, using the data for red phosphorus and liquid chlorine, are:

Na 0.97, Mg 1.75, Al 2.67, Si 2.49, P 2.14, S 2.06, Cl 1.33.

Of greater significance chemically are the related numbers representing the volumes in cubic centimeters occupied by a gram-atomic weight of each element (the **atomic volumes**):

Na 24, Mg 14, Al 10, Si 11, P 14, S 16, Cl 27.

A similar regular fluctuation is shown by all the physical properties of corresponding compounds.

Mendelejeff's Scheme. — In 1869 Mendelejeff published an important contribution towards adjusting the difficulty which the elements following chlorine presented, and developed the whole conception so completely that the resulting system of classification has been connected with his name ever since. Almost simultaneously Lothar Meyer made similar suggestions, but did not urge them with the same conviction or elaborate them so fully. The following table, in which the atomic weights are expressed in round numbers, is a modification of one of Mendelejeff's.

TABLE I. — ONE OF MENDELEJEFF'S TABLES, MODIFIED.

Li 7	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	Gl 9	B 11	C 12	N 14	O 16	F 19
Na 23	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	Mg 24.4	Al 27	Si 28.4	P 31	S 32	Cl 35.5
K 39	Ca 40	[Sc] 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 58.7	Cu 63.6	Zn 65.4	[Ga] 70	[Ge] 72.5	As 75	Se 79.2	Br 80
Rb 85.4	Sr 87.6	Y 89	Zr 90.6	Cb 94	Mo 96	. . .	Ru 101.7	Rb 103	Pd 106.5	Ag 108	Cd 112 4	In 115	Sn 119	Sb 120	Te 127.6	I 126.9
Cs 133	Ba 137.4	La 139	Ce 140	Di 145	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
. . .	. . .	Yb 173	. . .	Ta 183	W 184	. . .	Os 191	Ir 193	Pt 195	Au 197	Hg 200	Tl 204	Pb 207	Bi 208.5	. . .	. . .
. . .	Ra 225	. . .	Th 232.5	. . .	U 238.5	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .

The chief change from the arrangement in simple octaves is that the third series, beginning with potassium, is made to furnish material for two octaves, potassium to manganese and copper to bromine, and is called a *long series*. The valences fall in with this plan fairly well. Copper, while usually bivalent, forms also a series of compounds in which it appears to be univalent. Iron, cobalt, and nickel cannot be accommodated in either octave, as their valences are always two or three. At the time Mendelejeff made the table, three places in the third series had to be left blank, as a trivalent element [Sc] was lacking in the first octave, and a trivalent [Ga] and a quadrivalent one [Ge] in the second. These places have since been filled, as we shall presently see. The first two, (the *short*) series have been split in the table, as lithium and sodium closely resemble potassium, while the remaining members of these series fall more naturally over the corresponding elements of the second octave of the third series.

The fourth series (long) is nearly complete It begins with an active alkali metal, rubidium, and ends with iodine, a halogen. The rule of valence is strictly preserved throughout the series, and in general the elements fall below those which they most closely resemble.

The fifth, sixth, and seventh (long) series are incomplete, but the order of the atomic weights and the valence enable us satisfactorily to place those elements which are known. The chemical relations to elements of the fourth series justify the position assigned to each. Caesium, for example, is the most active of the alkali metals; barium has always been classed with strontium, and bismuth with antimony.

In two cases a slight displacement of the order according to atomic weights is necessary. Cobalt is put before nickel because it resembles iron more closely. Tellurium and iodine are placed in that order to bring them into the sulphur and halogen groups respectively. Their valence and other chemical relations both require this. The general agreement, however, is very remarkable.

General Relations in the System. — In every octave the valence towards oxygen ascends from one to seven, while that towards hydrogen, in the cases of the four last elements (when they combine with hydrogen at all), descends from four to one. The atomic volume disregards the subsidiary octaves in the long series. It descends towards the middle of each series (long or short), and ascends again towards its initial value. The other physical properties fluctuate within the limits of each series in a similar way. The values of each physical

constant for corresponding members of the successive series do not exactly coincide, however. A progressive change, as we descend each vertical column, is the rule. Thus the specific gravities (water = 1) of the alkali metals rise from lithium (0.59) to caesium (1.85). In the same group the melting-points descend from lithium (186°) to caesium (26.5°).

It must be stated that as yet no exact mathematical relation between the values for any property and the values of the atomic weights has been discovered; only a general relationship can be traced. Anticipating the discovery of some more exact mode of stating the relationship in each case, and remembering that similar values of each property recur periodically, usually at intervals corresponding to the length of an octave or series, the principle which is assumed to underlie the whole, the **periodic law**, is stated thus: **All the properties of the elements are periodic functions of their atomic weights.**

That the chemical relations of the elements vary just as do the physical properties of the simple substances is easily shown. Thus, each series begins with an active metallic (positive) element, and ends with an active non-metallic (negative) element, the intervening elements showing a more or less continuous variation between these limits. Again, the elements at the top are the least metallic of their respective columns. As we descend, the members of each group are more markedly metallic (in the first columns), or, what is the same thing, less markedly non-metallic (in the later columns; *cf.* p. 403).

In the first series boron is the first non-metal we encounter. In the second series silicon is the first such element. In the third there is more difficulty in deciding. Titanium, vanadium, and germanium are usually, though with questionable propriety, classed as metals. Selenium is undoubtedly a non-metal. Arsenic is, on the whole, a non-metal. In the fourth series tellurium is commonly considered to be the first non-metal. Thus a zigzag line, shown in the table, separates all the non-metals from the rest of the elements, and confines them in the right-hand upper corner.

A more compact form of the table, also based upon one of Mendelejeff's, may now be given (Table II). The only difference between this and the other is that the two octaves of each long series have been placed in the same set of seven main columns. The irregular sets of three elements, consisting of the iron, palladium, and platinum groups, occupy a column on the right of the main columns, and are often called collectively the eighth group. For completeness, the newly

TABLE II. — ONE OF MENDELEJEFF'S TABLES, MODIFIED.

E^0	E^ICl $E_2{}^IO$	$E^{II}Cl_2$ $E^{II}O$	$E^{III}Cl_3$ $E_2{}^{III}O_3$	$E^{IV}H_4$ $E^{IV}O_2$	$E^{III}H_3$ $E_2{}^VO_5$	$E^{II}H_2$ $E^{VI}O_3$	EH $E_2{}^{VII}O_7$	$E^{VIII}O_4$.
He = 4 Ne = 20	Li = 7 Na = 23	Gl = 9 Mg = 24.4	B = 11 Al = 27	C = 12 Si = 28.4	N = 14 P = 31	O = 16 S = 32	F = 19 Cl = 35.5	. . . .
A = 39.9	K = 39 Cu = 63.6	Ca = 40 Zn = 65.4	Sc = 44 Ga = 70	Ti = 48 Ge = 72.5	V = 51 As = 75	Cr = 52 Se = 79.2	Mn = 55 Br = 80	Fe = 56 Co = 59 Ni = 58.7
Kr = 87.8	Rb = 85.4 Ag = 108	Sr = 87.6 Cd = 112.4	Y = 89 In = 115	Zr = 90.6 Sn = 119	Cb = 94 Sb = 120	Mo = 96 Te = 127.6	. . . I = 127	Ru = 101.7 Rh = 103 Pd = 106.5
X = 128	Cs = 133 Au = 197	Ba = 137.4 Hg = 200	La = 139 Tl = 204	Ce, etc., 140–178 Pb = 207	Ta = 183 Bi = 208.5	W = 184 . . .	. . . . . .	Os = 191 Ir = 193 Pt = 195
. . . .	. . .	Ra = 225 ?	. . .	Th = 232.5	. . .	U = 238.5	. . .	. . . .

discovered elements, found chiefly in the air, have been placed at the left-hand side. Since they do not enter into combination at all, their valence may appropriately be given as zero. With the exception of argon, the values of their atomic weights agree well with this assignment. Hydrogen is the only element whose place is still in debate. Many rare elements have also been omitted, and tantalum has been placed immediately after cerium. The valence is shown by the general formulæ at the head of each column.

Applications of the Periodic System. — The system has found application chiefly in four ways:

1. By leading to the prediction of new elements.
2. By furnishing a comprehensive classification of the elements, arranging them so as to exhibit the relationships among the physical and chemical properties of the elements themselves and of their compounds. Constant use will be made of this property of the table in the succeeding chapters.
3. By enabling us to decide on the correct values for the atomic weights of some elements, when the equivalent weights have been measured, but no volatile compound is known (*cf.* pp. 201 and 212).
4. By suggesting problems for investigation.

The Prediction of New Elements. — Mendelejeff (1871) drew attention to the blank then existing between calcium (40) and titanium (48). He predicted that an element to fit this place would have an atomic weight 44 and would be trivalent. From the nature of the surrounding elements, he very cleverly deduced many of the physical and chemical properties of the unknown element and of its compounds. He named it eka-boron (Skr. *ēka*, one). In 1879 Nilson discovered scandium (44), and its behavior corresponded closely with that predicted for eka-boron.

In the same paper Mendelejeff described two other elements, likewise unknown at the time. They were to occupy vacant places between zinc and arsenic, and were named eka-aluminium and eka-silicon. In 1875 Lecoque de Boisbaudran found gallium, and in 1888 Winkler discovered germanium, and these blanks were filled. Other possible elements, such as eka-manganese and eka-antimony, were described, but still remain to be discovered.

Application to Fixing Atomic Weights. — Atomic weights have been fixed with the assistance of the periodic system on several occasions.

Thus the atomic weight of uranium was thought to be 120 until it was observed that no place near to antimony (120) remained unoccupied. With the value 240 (now 238.5), the element was accommodated at the foot of the column containing those which it most resembled. Again, the equivalent weight of indium was 38, and, as the element was supposed to be bivalent, it received the atomic weight 76. It was quite out of place near arsenic (75), however, being decidedly a metal. As a trivalent element with the atomic weight 115, it fell between cadmium and tin. Later work fully justified the change. Still again, glucinum, with equivalent weight 4.5, resembled aluminium so strongly that it was thought to be trivalent, like that element, and to have the atomic weight 13.5. But the only vacancy in the first series then existing was between lithium (7) and boron (11), and subsequent investigations showed that the properties of glucinum placed it most fittingly in that position as a bivalent metal with the atomic weight 9. Finally, and quite recently, radium (*q.v.*) has been discovered, and found to have the equivalent weight 112.5 and to resemble barium. If, like barium, it is bivalent, it occupies a place under this element, in the last series.

The System Suggests Lines of Investigation. — The periodic system has been of constant service in the course of inorganic research, and has often furnished the original stimulus to such work as well. For example, the atomic weights of the platinum metals at first placed them in the order, Ir (197), Pt (198), Os (199), although the resemblance to iron and ruthenium would have led us to expect that osmium should come first. For similar reasons platinum should have come last, under palladium. A reinvestigation of the atomic weights, suggested by these considerations, was undertaken by Seubert, and the old values were found in fact to be very inaccurate. He obtained: Os = 191, Ir = 193, Pt = 195.

Again, the atomic weight of tellurium bore the value 128 when the table was first constructed, and it was confidently expected that reexamination would bring this value below that of iodine (then 127, now 126.97). The problem has proved more difficult than usual, and several most careful studies of the subject have been made by chemists, using different methods. Absolute certainty has not yet been reached, but it seems probable that the real value of the atomic weight is not far from Te = 127.6, and therefore more than half a unit greater than that of iodine. Since, however, mathematical correspondence is found

nowhere in the system, the existence of marked inconsistencies like this need not shake our confidence in its value when it is used with due consideration of the degree of correspondence to be expected.

Originally lead, although it fell in the fourth column, possessed only one compound, PbO_2, in which it seemed to be undoubtedly quadrivalent. Search for salts of the same form, however, speedily yielded the tetrachloride ($PbCl_4$), tetracetate, and many others. As has been stated already, there are many elements between lanthanum and tantalum, about which sufficient knowledge has not yet been accumulated to make possible their definite allotment to places in the table. The existence of osmic acid (OsO_4), and a corresponding compound of ruthenium, suggests that other compounds of the elements of the eighth group, displaying the valence eight, may be capable of preparation. The collocation of copper, silver, and gold, in the same column with the alkali metals, is not at present perfectly satisfactory, and suggests the advisability of strengthening their position, if possible, by further investigation.

The System as a Guide in Classification. —Having disposed of the halogen and sulphur families, situated, respectively, in the seventh and sixth columns of the table, we shall next take up nitrogen and phosphorus from the right side of the fifth column. This family includes nitrogen, phosphorus, arsenic, antimony, and bismuth, and brings us for the first time in contact with a group which is partly non-metallic and partly metallic. Then from the fourth column, we shall select carbon and silicon, and from the third boron, leaving the other, more decidedly metallic elements for later treatment.

Exercises. — 1. Can you explain the presence of *free* selenium in the flues of pyrite-burners (p. 385)?

2. Why does the existence of tellurium tetrachloride in solution in aqueous hydrochloric acid show tellurium to be somewhat metallic in chemical properties?

3. How should you attempt to obtain HIO and $HBrO_4$, or their salts?

4. Make a list of bivalent elements and criticize this method of grouping as a means of chemical classification.

5. Write down the symbols of the elements in the fourth series of Table I (that beginning with rubidium, and ending with iodine). Record the valence of each element toward oxygen, using for reference the chapters in which the oxygen compounds are described.

CHAPTER XXIV

NITROGEN AND ITS COMPOUNDS WITH HYDROGEN

WHEN the oxygen of the air is removed (p. 62), a gas remains which is largely nitrogen. When first discovered, the most conspicuous property this gas was observed to have was indifference; it did not support combustion or life. The latter fact led to its being named *azote* (Gk. ζωτικός, life). While this name is still preserved in the French language, in English the name of the substance is derived from the fact that it is an important constituent of saltpeter KNO_3 (Lat. *nitrum*).

The Chemical Relations of the Element. — In some compounds nitrogen is trivalent, while in others, particularly those containing oxygen and other negative elements, it is quinquivalent.

The compounds of nitrogen are often extremely active and interesting. Those of them which we have to discuss in inorganic chemistry are ammonia (NH_3) and nitric acid HNO_3, and several related substances. The organic compounds containing nitrogen are very numerous and possess highly characteristic properties. Some, like nitroglycerine (*q.v.*) and gun-cotton, are violently explosive; others, like antipyrine, show great physiological activity; still others, such as the aniline and other organic dyes, provide us with beautiful and useful coloring matters.

Occurrence. — Apart from the presence of free nitrogen in the air, the element is found in many forms of combination. The nitrates of potassium and sodium are found in Bengal and Peru respectively. Natural manures, such as guano, contain large quantities of nitrogen compounds, and owe part of their value as fertilizers to this fact. Nitrogen is an essential constituent of vegetable and animal matter. The albumins, for example, which often make up a considerable part of such matter, contain on an average about 15 per cent of combined nitrogen.

Preparation. — Nitrogen containing about one per cent of argon (*q.v.*) is easily obtainable from purified air when the oxygen of the latter is removed. For this purpose phosphorus is frequently burned in the air, or the air is passed over heated copper.

When pure nitrogen is required, it must be obtained from chemical compounds, in order that it may be free from argon. The simplest method is to heat ammonium nitrite. This substance decomposes readily, even at temperatures little above the ordinary, according to the following equation:

$$NH_4NO_2 \rightarrow 2H_2O + N_2.$$

In practice, since ammonium nitrite cannot easily be kept, a mixture of an ammonium salt with some salt of nitrous acid is employed. Thus, when strong solutions of ammonium chloride and sodium nitrite are mixed, a double decomposition results in the formation of ammonium nitrite, $NH_4Cl + NaNO_2 \rightleftarrows NH_4NO_2 + NaCl$, and this breaks up when heat is applied, giving nitrogen.

In certain cases it is convenient to prepare nitrogen by the oxidation of ammonia (NH_3), by passing the latter over heated cupric oxide, or by the reduction of nitric oxide (NO) by passing this gas over heated copper.

Physical Properties. — Nitrogen is a colorless, tasteless, odorless gas, as we should expect from the fact that air possesses these properties. When sufficiently cooled, it forms a colorless liquid, boiling at $-194°$. By further cooling, this liquid freezes to a white solid, which melts at $-214°$. One liter of pure nitrogen weighs 1.2507 grams. The solubility of nitrogen in water: 1.6 volumes in 100, is less than that of oxygen.

Chemical Properties. — The density of the gas shows the formula of free nitrogen to be N_2.

Nitrogen unites with few common chemical elements directly. At ordinary temperatures it is almost absolutely indifferent. When passed through a tube over strongly heated lithium, calcium, magnesium, or boron, it forms definite chemical compounds, known as nitrides, in which it is trivalent. These have the formulæ Li_3N, Ca_3N_2, Mg_3N_2, and BN respectively. When the gas is mixed with oxygen or hydrogen, and the mixture is heated, little chemical action takes place. When sparks from an induction coil are passed between platinum

wires through the mixtures, small amounts of nitrogen tetroxide N_2O_4, and ammonia NH_3, respectively, are produced. The indifference of free nitrogen is doubtless due to the fact that its molecules (N_2) are extremely stable.

One case of direct union of nitrogen is of economic importance. The supply required by plants is obtained partly from nitrogen compounds contained in fertilizers, or equivalent substances already present in the soil, and partly from ammonium nitrite and nitrate, which are washed down from the air by the rain. It appears, however, that plants belonging to the order *leguminosæ*, such as peas, beans, clover, etc., may be associated constantly with certain bacteria which flourish in nodules upon their roots. These bacteria have the power of taking free nitrogen from the air, which penetrates the soil, breaking up its molecules, and producing compounds containing nitrogen. The masses round the roots often contain over five per cent of combined nitrogen which has been acquired in this way. These compounds are chiefly albumins, which are afterwards digested and absorbed by the roots of the plant.

Compounds of Nitrogen and Hydrogen. — The commonest and longest known of these substances is ammonia NH_3, which was first described by Priestley (1774) and named "alkaline air." Curtius discovered hydrazine N_2H_4 in 1889, and hydrazoic acid HN_3 in 1890. Hydroxylamine NH_3O, discovered by Lossen in 1865, is similar to ammonia in chemical behavior.

Ammonia.

Ammonia is liberated in connection with the putrefaction of animal matter.

Preparation. — 1. When sparks from an induction coil are passed through a mixture of nitrogen and hydrogen, small proportions of the materials unite to form ammonia (see below).

2. When water is added to the nitride of magnesium or calcium (p. 416), ammonia is given off and the hydroxide of the metal formed:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3.$$

3. When parts of animals, particularly the horns, hides, and feathers, which contain complex compounds of carbon, nitrogen, hydrogen, and oxygen, are heated strongly, much of the nitrogen is driven out as

ammonia. Hence the name *spirit of hartshorn*, applied to the aqueous solution.

4. Coal often contains as much as 2 per cent of combined nitrogen, and when heated in absence of air, gives off much ammonia. The entire commercial supply is obtained as a by-product from operations like the manufacture of illuminating-gas and of coke, in which the destructive distillation of coal takes place. The crude mixture of gases passes first through water, in which some of the tar is condensed and most of the ammonia dissolves. This *ammoniacal liquor* is heated with a little slaked lime, and the escaping gas is led into dilute hydrochloric or sulphuric acid, with which it combines to form the chloride or sulphate of ammonium.

5. In the laboratory, a mixture of slaked lime and some salt of ammonium, such as ammonium chloride, either with or without water, is heated in a flask or retort provided with a delivery tube:

$$Ca(OH)_2 + 2NH_4Cl \leftrightarrows CaCl_2 + 2NH_4OH,$$
$$NH_4OH \rightleftarrows H_2O + NH_3.$$

By the double decomposition usual with ionogens, ammonium hydroxide is formed, and this, being unstable, immediately breaks up into water and ammonia.

6. Warming the aqueous solution also gives a steady stream of the gas. Since the gas is very soluble in water, it must be collected over mercury or by upward displacement of air. The moisture which it may contain is removed by passage through a tower or wide tube filled with quicklime. Calcium chloride cannot be used, as the gas combines with it forming a compound $CaCl_2, 8NH_3$, similar in properties to a hydrate (pp. 120–123).

Physical Properties. — Ammonia is a colorless gas with a pungent, characteristic odor familiar in smelling-salts. The G.M.V. of the gas weighs 17.29 g., so that the density is little more than half that of air (*cf.* p. 215) When liquefied it boils at $-34°$ and exercises a pressure of 6.5 atmospheres at 10°. The solid is white and crystalline and melts at $-77°$. The gas is very soluble in water, one volume of the latter dissolving 1148 volumes of the gas at 0°, 764 volumes at 16°, and 306 volumes at 50°. The 35 per cent aqueous solution, saturated at 15°, and sold as "concentrated ammonia," has a sp. gr. 0.882. The whole of the dissolved gas may be removed by boiling (*cf.* p. 379).

Liquefied ammonia is used in refrigeration. The gas is liquefied by compression, and the heat which is thus liberated is removed by flowing water which surrounds the pipes. The liquid then flows into other pipes immersed in calcium chloride brine, and is there allowed to evaporate, the gas returning to the compressor. The heat of vaporization, 260 calories per gram, is taken from the brine, which is thus partially frozen. The resulting freezing mixture of ice and calcium chloride solution is then distributed to the localities to be cooled. The ammonia and brine remain within their respective closed systems of pipes, and are used over and over again. In many cases the cooling by the liquefied ammonia is used directly, and the intermediate freezing mixture is dispensed with.

Chemical Properties. — The discharge from an induction-coil decomposes ammonia (to the extent of 94–98 per cent) into nitrogen and hydrogen. Under the same circumstances, union of the constituents also occurs (up to 2–6 per cent) :

$$2NH_3 \leftrightarrows N_2 + 3H_2.$$

The behavior of a system in chemical equilibrium may be illustrated by inclosing dry ammonia in a tube over mercury and allowing sparks to pass between platinum wires (Fig. 85). After a time the volume is practically doubled, every two molecules of ammonia giving four of the products (*cf.* p. 208). When, now, a little sulphuric acid is admitted above the mercury, the remaining trace of ammonia combines with the acid and is removed. This disturbs the equilibrium. As sparks continue to pass, the action now proceeds steadily backwards. The ammonia which is formed is no longer subject to decomposition, for, once it has combined with the acid, it never returns to the neighborhood of the discharge. Thus the whole of the gases finally combine :

$$(NH_4)_2SO_4 \leftarrow H_2SO_4 + 2NH_3 \leftrightarrows N_2 + 3H_2,$$

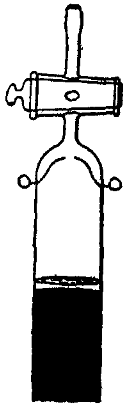


FIG. 85.

and ammonium sulphate, dissolved in the excess of acid, alone remains. The action, therefore, first goes almost completely in one direction, and then quite completely in the other, while no change has taken place in the conditions to which the gas is subjected at the point where the interaction is occurring. The sole

difference is that a little of an acid has been introduced into a relatively remote part of the space.

When passed over reducible oxides, such as heated cupric oxide, ammonia is oxidized to water and free nitrogen:

$$3CuO + 2NH_3 \rightarrow 3Cu + 3H_2O + N_2,$$

and burns in pure oxygen with the same result. In air, heat is used up, not only in decomposing the compound, but also in raising the temperature of the nitrogen of the atmosphere. This causes a continuous drain on the heat given out by the action, and prevents the maintenance of the kindling temperature (p. 73).

When dry ammonia is passed over heated potassium or sodium, one unit of hydrogen is displaced:

$$2K + 2NH_3 \rightarrow 2KNH_2 + H_2,$$

and a solid of metallic appearance remains behind. Substances containing the group $-NH_2$ are called amides, and this one is therefore named **potassamide.**

Chlorine and bromine combine with the hydrogen and liberate the nitrogen of ammonia. This action may be used for obtaining a stream of nitrogen, provided excess of chlorine is avoided (see Nitrogen trichloride, below). Chlorine is led into a solution of ammonium chloride:

$$2NH_4Cl + 3Cl_2 \rightarrow N_2\uparrow + 8HCl.$$

The most characteristic property of ammonia is its power to form a base by combination with water:

$$NH_3\ (gas) \leftrightarrows NH_3\ (diss'd) + H_2O \rightleftarrows NH_4OH \leftrightarrows NH_4^{\cdot} + OH'.$$

Probably only a small proportion of the gas is actually combined at any one time, the greater part being simply dissolved.

The gas unites also with acids, forming salts (*cf.* p. 337), which, in solution, are highly ionized:

$$NH_3 + HCl \rightarrow NH_4Cl,$$
$$NH_3 + HNO_3 \rightarrow NH_4NO_3.$$

Ammonium Compounds. — Since NH_4 plays the part of a metal, entering into the composition of a base and of a series of salts, it is named **ammonium.** It constitutes the positive ion of these compounds. As this radical forms a univalent ion and gives a distinctly alkaline base, it is classed with potassium and sodium as one of the metals of the alkalies (*q.v.*).

Ammonium hydroxide, although much less completely ionized than potassium hydroxide, affects litmus easily. In a normal solution about 0.4 per cent of the ammonia is in the form of ammonion, $NH_4^{\cdot}$. When an acid is added to the solution, the correspondingly small amount of hydroxidion which exists in it is removed and the various equilibria are displaced forwards. The final result is the same as with any other base:

$$\left.\begin{array}{r} NH_3\ (\text{diss'd}) + H_2O \rightleftarrows NH_4OH \leftrightarrows NH_4^{\cdot} + OH' \\ 2HCl \leftrightarrows 2Cl' + 2H^{\cdot} \end{array}\right\} \leftrightarrows H_2O.$$

When strongly heated, all ammonium salts are decomposed and, usually, give ammonia and the acid. When the latter is volatile, the whole material of the salt is thus converted into gas. If the acid is volatile without permanent decomposition, it reunites with the ammonia when the vapor is cooled:

$$NH_4Cl \rightleftarrows HCl + NH_3.$$

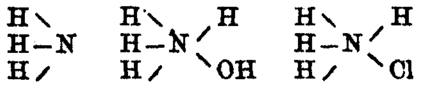
This behavior distinguishes ammonium salts from those of the typical metals, for, with the exception of mercury salts, most other salts are not easily and completely volatilized. The use of ammonium chloride (sal-ammoniac) in **soldering** depends on the dissociation of the salt, by the heat of the iron, and the action of the liberated hydrochloric acid on the oxide which covers the surface of the metal to be soldered.

Ammonium salts are **recognized** by warming them, dry or in solution, with a base:

$$\left.\begin{array}{l} (NH_4)_2SO_4 \leftrightarrows SO_4'' + 2NH_4^{\cdot} \\ 2KOH \ \leftrightarrows \ 2K^{\cdot} + 2OH' \end{array}\right\} \leftrightarrows 2NH_4OH \rightleftarrows 2H_2O + 2NH_3 \uparrow$$

when the odor of ammonia becomes noticeable. When the solution is used, it is the tendency of the $NH_4^{\cdot}$ and OH' to unite to form the slightly ionized molecular hydroxide that sets the other equilibria in motion. The principle at the basis of the change is thus the same as in neutralization (p. 354).

In ammonia, nitrogen is trivalent, while in the salts it appears to be quinquivalent:



HYDRAZINE, HYDRAZOIC ACID, HYDROXYLAMINE.

Hydrazine. — By reduction of a compound of nitric oxide and potassium sulphite by means of sodium amalgam,* a solution of hydrazine hydrate is obtained :

$$K_2SO_3, 2NO + 6H \rightarrow N_2H_4, H_2O + K_2SO_4.$$

The same substance is more easily made from certain organic derivatives. When the hydrate is distilled with barium oxide, under reduced pressure, hydrazine is liberated :

$$N_2H_4, H_2O + BaO \rightarrow N_2H_4\uparrow + Ba(OH)_2.$$

Hydrazine is a white solid, which fumes in moist air, giving the hydrate once more. It melts at 1.4° and boils at 113.5°.

Hydrazine hydrate freezes at about −40°, boils at 118.5°, and can be distilled without decomposition. Its aqueous solution is alkaline, and salts can be formed by neutralization.

Hydrazoic Acid. — When nitrous oxide (*q.v.*) is led over sodamide at 200°, water is liberated and sodium hydrazoate remains behind :

$$NH_2Na + N_2O \rightarrow NaN_3 + H_2O.$$

A dilute solution of the free acid is best obtained by distilling the lead salt with dilute sulphuric acid. A similar solution may be made more directly by adding cold nitrous acid (*q.v.*) to a cold aqueous solution of hydrazine hydrate :

$$N_2H_5OH + HNO_2 \rightarrow HN_3 + 3H_2O.$$

By repeated distillation of the solution the pure acid is obtainable. It boils at 37°. The operation is a dangerous one, as the pure acid is violently explosive, resolving itself into nitrogen and hydrogen with liberation of much heat :

$$HN_3, Aq \rightarrow H + 3N + Aq + 61,600 \text{ cal.}$$

It is an acid of somewhat greater activity and degree of ionization than acetic acid. Active metals, like magnesium, displace hydrogen from its solution. Its silver salt (AgN_3) is insoluble in water. It neutral-

* The sodium dissolved in the mercury interacts with the water, giving hydrogen (see Active state of hydrogen, below).

izes ammonium hydroxide and hydrazine hydrate, giving two salts, NH_4N_3 and $N_2H_5N_3$. These constitute two additional compounds of nitrogen and hydrogen, but differ from ammonia and hydrazine in being ionogens.

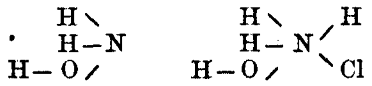
Hydroxylamine. — Tin displaces hydrogen from dilute hydrochloric acid: $Sn + 2HCl \rightarrow SnCl_2 + H_2$, and this combination forms a reducing agent (see below). When dilute nitric acid (*q.v.*) is added to the mixture, a considerable part of it is reduced to hydroxylamine:

$$HNO_3 + 6H \rightarrow NH_3O + 2H_2O.$$

The hydroxylamine forms a weak base, $NH_4O.OH$, with water which interacts with the excess of acid, giving hydroxylamine hydrochloride, NH_4OCl. By more complete reduction of part of the nitric acid, some ammonium chloride is formed at the same time. To secure the salt of hydroxylamine, the tin ions are removed by means of hydrogen sulphide, which precipitates stannous sulphide. The filtered solution is then evaporated to dryness, the hydroxylamine hydrochloride is extracted from the residue with absolute alcohol, and this alcoholic solution is finally evaporated in turn. The hydrochloride is a white crystalline salt.

When the hydrochloride is treated with a base, in the absence of water, and the mixture is distilled under reduced pressure, hydroxylamine passes over. It is a white solid melting at 33° and boiling at 58° at 22 mm. pressure. Even before melting (above 15°), it begins to decompose, and explodes at or below 130°. In chemical behavior it is like ammonia. With water it forms a base which combines with acids, but is less active than ammonium hydroxide. It is a stronger reducing agent than ammonia, precipitating silver from a solution of silver nitrate.

The union with acids indicates that the molecule of hydroxylamine is unsaturated, and hence the nitrogen unit is supposed to be trivalent:



An Active State of Hydrogen (Nascent Hydrogen). — Pure hydrogen gas, whatever its source may have been, shows conspicuous reducing powers only when heated (*cf.* p. 109). But when the gas is absorbed in platinum or palladium (p. 107), the two together reduce many substances in the cold, although the platinum and palladium themselves seem to take no part in the change. They are simply

catalytic or contact agents, and in their presence the hydrogen is more active. Similarly the hydrogen liberated by the electrolysis of a dilute acid reduces substances added to the liquid surrounding the cathode (*cf.* p. 304), and shows different degrees of activity according to the material, platinum, carbon, or the like, of which the cathode is made. Finally, zinc, tin, and other metals with dilute acids give hydrogen, and this can produce reductions so long as it is in the immediate neighborhood of the metal (*cf.* pp. 422, 423, and see Arsine). Thus, as we have just seen, nitric acid is reduced to hydroxylamine when it is mixed with the materials which generate the hydrogen. The hydrogen on the platinum plate forming the cathode of an electrolytic cell is equally able to reduce nitric acid. The very same hydrogen, however, if led by a tube *from* a Kipp's apparatus or electrolytic cell into a second vessel would be then quite inactive and incapable of affecting the same nitric acid. Hydrogen, therefore, like other substances, may show a greatly increased speed of interaction when in immediate contact with a suitable body. This **more active** state of hydrogen is described as the **nascent state**, because it happens to be a common condition of hydrogen when associated with substances which produce it. This state has, however, no necessary connection with such an immediately preceding act of liberation, as our first example shows.

Some theorists apply the atomic hypothesis to this phenomenon, and suggest that it is the freshly liberated atomic hydrogen (H) which possesses this greater activity. This would require us to believe that nascent hydrogen was a different substance from free hydrogen, which may or may not be true, but is certainly improbable. If the hypothesis of atomic hydrogen were correct, all arrangements that give free hydrogen under similar circumstances (*e.g.* electrolytic cells with different electrode-materials) should show equal reducing powers. But it is notorious that they do not. Different substances are known, however, to show different efficiencies as contact agents.

The atomic theory of nascent action is often used to explain the oxidizing activity of hypochlorous acid (*cf.* p. 271). But it is less often employed to explain the oxidizing power of sulphuric acid or other oxidizing agents. Yet, logically, it ought to be applied even to double decomposition, if it is used at all. If this were done, salt and sulphuric acid would be assumed to give nascent chlorine and nascent hydrogen, respectively, since they yield hydrogen chloride in the cold, while free hydrogen and chlorine do not.

Halogen Compounds of Nitrogen. — When ammonium chloride solution is treated with excess of chlorine, drops of an oily liquid, **nitrogen trichloride**, are formed:

$$3Cl_2 + NH_4Cl \rightarrow NCl_3 + 4HCl.$$

It is extremely explosive, resolving itself into its constituents with liberation of much heat.

There appear to be several compounds related to ammonia and containing iodine. When a solution of iodine in potassium iodide solution (p. 156) is added to aqueous ammonia, a brown precipitate is formed. This seems to have the composition $N_2H_3I_3$, and is named **nitrogen iodide.** It may be handled while wet, but when dry decomposes into its constituents with violent explosion if touched with a feather.

Exercises. —1. When moist air is used as a source of nitrogen, what advantage is there in using copper rather than the less expensive metal iron, for removing the oxygen (p. 416)?

2. How many grams of water at 0° could be frozen (p. 115) by the removal of the heat required to evaporate 50 g. of liquid ammonia (p. 419)?

3. How many grams of ammonia are contained in 1 l. of "concentrated ammonia" (p. 418)?

4. What are the ions of hydrazine hydrate (p. 422)? Formulate (p. 454) the neutralization of this base with sulphuric acid.

5. What is the object attained by distilling under reduced pressure in making hydrazine (p. 422) and hydroxylamine (p. 423)?

6. Classify (p. 187) the interaction of a nitride with water (p. 417), and of chlorine and ammonium chloride (p. 420), and the results of heating ammonium nitrite (p. 416) and ammonium chloride (p. 421).

CHAPTER XXV

THE ATMOSPHERE. THE HELIUM FAMILY

We have seen that to counterbalance the pressure of the air a column of mercury of the same diameter averaging 760 mm. in height is required. Let the section of the column be 1 sq. cm. Then the pressure of a column of air 1 sq. cm. in section, and extending so far from the earth as any downward tendency of the air exists, is equal to the weight of a column of mercury containing 76 c.c. of the metal. The weight of 1 c.c. of mercury being 13.6 g., this volume of the metal weighs 1033.6 g. This number represents therefore the pressure which is exerted by the air upon each square centimeter of the earth's surface. In ordinary units of measure, this is nearly fifteen pounds to the square inch.

A more vivid appreciation of the reality of this pressure may be obtained by noticing one of its effects. By boiling a small quantity of water in a tin can furnished with a narrow opening, we remove the whole of the air from its interior, displacing it by steam. While the boiling is in progress, we suddenly close the opening with a tightly fitting cork and remove the burner. While the steam was still issuing from the opening, its pressure was practically that of the atmosphere, and the can was subject to the same pressure inside and out. With the removal of the flame, however, the steam condenses, and the pressure on the interior is reduced to a minute fraction of its original value, while the pressure on the exterior is still the same (1 atmosphere). Under this pressure a vessel of ordinary tin-plate completely collapses.

Components of the Atmosphere. — The first component of the air to be recognized and studied was oxygen. When a rusting metal or burning body of any kind removes the oxygen by combining with it, a gas remains which represents about four-fifths of the original volume. This residual gas is mainly nitrogen. It contains, however, small proportions of several inert gases, of which the most plentiful is argon. Examination before the removal of the oxygen also reveals the presence of varying proportions of carbon dioxide, water vapor, and ammonium nitrate. In the neighborhood of cities the air likewise contains sulphur dioxide, hydrogen chloride, hydrogen sulphide, and other ingredients which may be described as accidental. There are thus three classes

of substances in the air. Those of the first class, oxygen, nitrogen, and argon, are present in almost constant quantities; those of the second class are very variable in quantity, although found in all samples of air; those of the third class are accidental. Finally, one significant component of the air is the dust which a powerful beam of light reveals as it passes through the atmosphere of a darkened room.

Components which are Constant in Amount. — The determination of the **oxygen** by burning phosphorus in air, and measuring the residual gas (p. 416), is not capable of application in an exact manner. It is better to use a large amount of phosphorus in the form of thin wire. In this way a great surface is obtained, and the absorption of oxygen from a sample of air may be carried out in a few seconds. This method gives fairly accurate results, since there is no time for any appreciable change in the temperature or pressure of the atmosphere during the experiment. The passage of purified air over heated copper (p. 416) has also been used for the same purpose. When this method is employed, the volume of the nitrogen and argon which survives the action of the copper is measured, while the increase in weight of the copper, through formation of cupric oxide, gives the weight of the oxygen which was originally mixed with it.

Still another method, which is in constant employment in the analysis of mixtures of gases, may also be applied to the air. It consists in mixing a measured volume of air with an excess of hydrogen, reading off the volume of the whole, and then exploding the mixture by the passage of an electric spark. A tube like that in Fig. 44 (p. 125) may be used. After the explosion, the steam which has been formed condenses. The contraction gives the volume of the gases which have disappeared through the explosion, and of this one-third is oxygen and two-thirds hydrogen (*cf.* p. 125). When, for example, a contraction of 25 c.c. of gas has occurred, we know that one-third of this volume (namely, 8.3 c.c.) is the volume of oxygen which the measured sample of air contained.

In the air taken from mines, from mountain tops, from the surface of the sea, and from inland regions, the proportion of oxygen to the residual gas is found to be fairly constant, although easily perceptible differences are noted. The percentage of oxygen in dried air ranges between 20.26 and 21.00, the latter being the proportion in normal air.

When the residual gas is led slowly through a heated tube con-

taining magnesium, the **nitrogen** unites with the metal to form the solid nitride (p. 416), and only about 10 c.c. out of every liter remains uncombined. This residuum is **argon**, mixed with one-hundredth of its volume of other gases belonging to the same family (see below). Exact measurement by volume gives 78.06 per cent of nitrogen and 0.94 per cent of argon in dried air.

It is possible that a trace of hydrogen (*cf.* p. 92) is one of the regular components of air.

Components which are Variable in Amount. — Pure country air contains about 3 parts in 10,000 of **carbon dioxide**. In city air there are from 6 to 7 parts in the same volume, while in the air of audience-rooms, where the ventilation is defective, the proportion may rise as high as 50 parts.

The simplest way of showing the presence of carbon dioxide in the air is by exposing a solution of barium hydroxide in a shallow vessel. After a short time a layer of barium carbonate forms upon the surface, in consequence of a chemical change represented by the equation, $Ba(OH)_2 + CO_2 \rightarrow BaCO_3 \downarrow + H_2O$. The same action may be utilized for the purpose of quantitative analysis. A measured volume of air is bubbled slowly through a measured volume of a solution of barium hydroxide of known concentration, and the quantity of barium hydroxide remaining is determined by titration (p. 352).

The sources of the carbon dioxide in the air are numerous. It comes from the decay of vegetable and animal matter, in which, chiefly through the influence of minute vegetable organisms, the carbon is oxidized to carbon dioxide. It is formed also by the combustion of coal and wood, and is exhaled by animals. The proportion of this gas in the air would naturally increase continuously, though slowly, as the result of these processes, were it not that it is removed just as continuously by the action of growing plants (see Chap. xxviii). Thus, there is no reason to suppose that the proportion of carbon dioxide in the air will be altered appreciably, the two kinds of operations probably balancing one another approximately.

The quantity of **water vapor** in the air is constantly changing. It increases locally by evaporation from the soil and from natural waters, particularly in warm weather. It decreases when local cooling leads to the precipitation of water in the forms of mist and rain. The phrase commonly heard, that on a moist day the atmosphere is "laden" with moisture, is peculiarly inapt. We recognize at once from obser-

vation of the barometer, which is lower in such a state of the atmosphere, that the pressure of the air is less. Moist air must be lighter than dry air, for in it a certain proportion of water molecules, of molecular weight 18, is substituted for an equal number (*cf.* p. 190) of molecules of nitrogen and oxygen whose relative weights are 28 and 32 respectively. The result is therefore a diminution in the specific gravity of the air. The proportion of water in a given volume of air may be measured most accurately by permitting the air to stream slowly through tubes filled with calcium chloride or phosphoric anhydride (Fig. 36, p. 100). The increase in weight of the charged tubes represents the quantity of moisture abstracted from the sample.

The **ammonium nitrate** arises from the interaction of nitric acid and ammonia. The latter is formed by the decay of animal matter (p. 417); the former by the union of nitrogen and oxygen during thunder-storms. The electrical discharges produce nitrogen tetroxide (see p. 439), which with water gives nitric acid (*q.v.*).

The **dust** varies both in kind and quantity according to the locality. It is found to be partly inorganic. In the country the nature of the inorganic material depends upon the prevailing components of the soil, and in factories the dust may consist of minute particles of glass, steel, cement, or other substances. The organic dust may be divided into two kinds. The part which is dead includes coal dust, refuse from the streets, minute shreds of cotton, linen, hay, etc. The living dust consists of pollen grains, spores of fungi and other plants, germs of infusoria, and bacteria. The presence of such germs in the air is shown by the fact that when nutritive liquids have been exposed to the air, even for a few minutes, putrefaction very soon sets in. Some of these germs also produce disease when they gain access to the body, particularly through wounds, or incisions made in the course of operations. The object of antiseptic treatment by the use of phenol (carbolic acid), mercuric chloride, and other substances, is to destroy such organisms or to hinder their development.

Flasks can be filled with dustless air through the displacement of that which they contain by air drawn through a wide tube packed with 12–15 inches of cotton. It has been shown by Aitken that air of this kind behaves differently from ordinary air in respect to the way in which its moisture condenses.

If a sample of moist air is cooled until it contains more water vapor than it could take up at the existing temperature, the excess of moisture is deposited. This deposition usually takes place by the forma-

tion of a multitude of little particles of liquid water, which together make up a fog. Now dustless air lacks this property entirely. When saturated with water and then cooled, it does not give any trace of fog. The excess of moisture is gradually deposited upon the walls of the vessel and upon any material objects which it contains, but of fog there is no trace visible. It seems that the particles of dust are required as nuclei round which the water may gather. In the absence of dust, and therefore of proper nuclei, the moisture is not precipitated in the usual way. Thus fogs and rain would be impossible but for the presence of dust in all ordinary air.

By diluting air with dustless air, generating fog in the mixture, and, with the help of a microscope, counting the globules when they settle, an estimate of the number of particles of dust in air may be made. It is found that rain removes a large proportion of them, while respiration and combustion greatly increases their number. The prevalence of fogs in cities is thus accounted for.

	Number of Dust Particles in 1 c.c.
Outside, raining	32,000
Outside, fair	130,000
A room	1,860,000
A room, near the ceiling	5,420,000
Air above Bunsen flame	30,000,000

Air a Mixture. — Since the main components of air were not definitely identified until the end of the eighteenth century, we can understand why the substance was for long considered to be an element. The experiments which we have described, in which the oxygen was removed from the air and the nitrogen remained, do not prove that the original constituents were present simply in mechanical mixture. They might have been combined, and the combustion of phosphorus, for example, might have represented the removal of oxygen from combination with nitrogen and its appropriation by the phosphorus. It may be well, therefore, to point out some reasons which lead us to regard the air as a mixture:

1. When oxygen and nitrogen are mixed in the proper proportions, we obtain a gas identical with air in all its properties, and there is no evidence of any production or absorption of heat, such as would occur in case of chemical combination.

2. The proportion by volume in which the gases are found in the air is not so simple as the proportions which we observe in cases of chemical combination. The proportion is close to 4 : 1, but not exactly 4 : 1. Besides, as we have seen, the proportion is not perfectly constant.

3. The composition of air varies, while the composition of definite chemical substances is always the same. The proportions by weight also in which the components are contained in air are not integral multiples of the atomic weights.

4. When two substances enter into chemical combination, the new body invariably has different physical properties from either of the original ones. Thus, there is no simple relation between the refractive power for light which a compound possesses and the refractive powers of its constituents. In the case of air, however, the refractive power is exactly that which we should calculate from the refractive powers of the constituents, taking into account the proportions of them which air contains. The same relation holds for all ordinary physical properties of air. For example, the nitrogen and oxygen dissolve independently in water in proportion to their solubilities and partial pressures (p. 155). If the air were a compound, it would dissolve as a whole, and the relative proportions of the components would not be changed by the process.

Composition of Air. — Air, when freed from carbon dioxide and water, contains by volume 78.06 per cent of nitrogen, 21.00 per cent of oxygen, and 0.94 per cent of argon. When only the water is removed, the carbon dioxide averages about 0.03 per cent of the whole.

Graham has suggested an illustration which will make those proportions clearer. He says that if we imagine the air to be divided by magic into its components, and to remain separated for a time sufficiently long to enable us to note the proportions, and if the substances arrange themselves in the order of their specific gravities, we should have the following layers resting upon the surface of the earth and upon one another: On the earth, five inches of water; above that, thirteen feet of carbon dioxide; above that, a mile of oxygen; and on the top, about four miles of nitrogen. This would be on the assumption that these gases were compressed so as to have the same density throughout. The recent discovery of argon shows that we should add to this illustration a layer of argon, of about ninety yards thickness, between the carbon dioxide and oxygen.

Air and Health. — As human beings we have an especial interest in the composition of the air, since our living depends upon the oxygen which we secure by breathing it. We draw about half a liter of air into our lungs at each breath, or about half a cubic meter per hour. The oxygen of this air is partly used, being taken up by the blood, and part remains in the exhaled air. On the other hand, carbon dioxide is given off in the lungs and passes out with the unused oxygen. The nitrogen is unaffected. In 100 c.c. of expired air there are contained about 15.9 c.c. of oxygen and 3.7 c.c. of carbon dioxide. The total quantity of oxygen consumed during twenty-four hours is about three-fourths of a kilogram, or more than half a cubic meter. While the greater part of this gains access to the body through the lungs, more or less exchange of gases takes place in all animals through the skin.

The lower limit of oxygen for respirable air is about 10 per cent, although a candle is extinguished if the proportion falls below 16.5 per cent. The union of oxygen or carbon dioxide with the hæmoglobin of the red blood-corpuscles is a reversible reaction. In the tissues, where the concentration of oxygen is small and that of carbon dioxide large, *the former leaves the hæmoglobin and the latter combines with* it. Conversely, in the lungs, where the concentration of oxygen is at a maximum, and that of carbon dioxide at a minimum, the reverse changes occur.

Liquefaction of Gases. — The earliest experiments of this kind seem to have been made by Northmore (1805), who liquefied chlorine, hydrogen chloride, and sulphur dioxide. In 1823 chlorine was again liquefied by Faraday; and in the same year Davy, whose assistant Faraday was, liquefied hydrogen chloride. During the following years Faraday reduced other gases — sulphur dioxide, hydrogen sulphide, carbon dioxide, nitrous oxide, cyanogen, and ammonia — to the liquid condition.

The method which he employed was extremely simple. He used a bent tube shaped like an inverted v (Λ), into one limb of which materials for producing the gas were introduced. The other limb was then sealed up and immersed in a freezing mixture. The gas, usually liberated by heating, was liquefied by its own pressure in the cold limb. By means of a more elaborate apparatus, Cailletet and Pictet simultaneously (December, 1877) obtained, the one, a fog, and the other, a spray containing droplets of liquid oxygen. In 1883 Wroblewski and Olszewski made larger amounts of the same liquid. About

the same time Dewar devised means of manufacturing large quantities of liquid air and oxygen.

The principle now used in liquefying gases depends on the fact that a *perfect* gas, when expanding into a vacuum, should suffer no fall in temperature, since it does no work, while ordinary gases do become cooled very slightly. The work which they do in expanding in such circumstances is done in overcoming the cohesion between their molecules (p. 131), and occasion for it arises from the fact that a tearing apart of the substance, which consumes heat, has to take place. Since this cohesion becomes more conspicuous the lower the temperature (*cf.* p. 135), the cooling effect of expansion becomes greater and greater as the temperature falls.

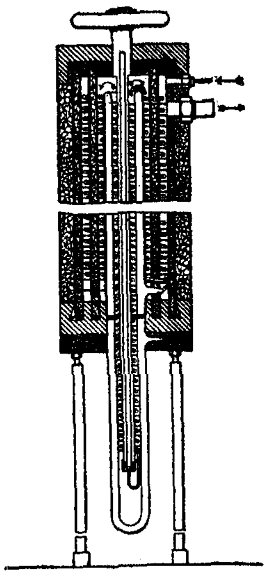


Fig. 86.

By ingenious arrangement of the apparatus, the low temperature produced by the expansion of the compressed gas is used to cool fresh portions of the gas which have not yet been expanded. The tube containing the compressed gas is placed concentrically within another tube, and the stream of gas after it has expanded is turned back upon its course and passes through the annular space along the tube containing the unexpanded gas. This double tube is many yards long, so that the most perfect contact and complete interchange of heat can occur. Thus, by a process of intensification, the temperature of the unexpanded gas is continually depressed, and the temperature after expansion, therefore, becomes lower still. Finally, the latter temperature becomes low enough to produce liquefaction of the compressed gas at the pressure to which it is subjected, and the jet of expanding gas is filled with drops of liquid. These are caught in a recess of the vessel, and may be removed from time to time through a stopcock.

The most successful apparatus for use on a small scale is that devised by Hampson (Fig. 86). The compressed gas enters by the small tube near the top, and eventually issues by the wider one. The inner tube is coiled in a small cylinder to secure compactness, and a spiral

partition between the coils produces the outer tube of which we have spoken. The gas in the tube *A* (Fig. 87) is under a pressure of 150–200 atmospheres. The distance of the nozzle *D* from the plug *C* is adjusted so that the pressure of the gas in the chamber and spiral outer tube is reduced to one atmosphere.

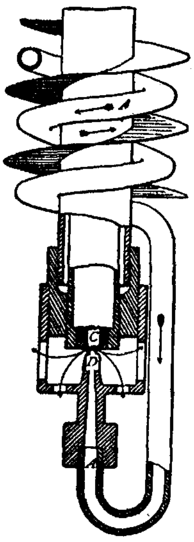


FIG. 87.

For handling liquefied gases, a form of apparatus devised independently by Weinhold and Dewar is employed (Fig. 88). It consists of a double flask in which the space between the inner and outer bulbs has been exhausted by means of an air-pump. To prevent by reflection the access of radiant heat to the interior, the surfaces of the flasks are often silvered.

Liquid Air.—Liquid air varies in composition, as the nitrogen (b.-p. – 194°) is less condensible than the oxygen (b.-p. – 182.5°). It boils at about – 190°, and contains about 54 per cent of oxygen by weight, while air contains 23.2 per cent. By allowing evaporation to go on, a liquid containing 75 to 95 per cent of oxygen is easily obtained (*cf.* p. 63). The gas secured by the evaporation of the residue is pumped into cylinders and sold as compressed oxygen. Cartridges made of granular charcoal and cotton waste, when saturated with liquid air, have been used as an explosive in mining.

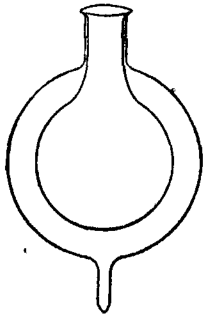


FIG. 88.

THE HELIUM FAMILY.

Argon.—Lord Rayleigh was the first to observe that, while specimens of oxygen and other gases made purposely from various sources always had the same density, nitrogen was an exception. One liter of nitrogen made from air, and supposed to be pure, weighed 1.2572 g. When the gas was manufactured by decomposition of five different compounds, such as urea and certain oxides of nitrogen, the results agreed well amongst themselves. The mean weight of a liter of this nitrogen was only 1.2505 g. The difference, amounting to nearly

7 mg., was very much greater than the experimental error. The suspicion naturally arose that some heavier gas was present in natural nitrogen. Soon after (1894), Professor, now Sir William Ramsay obtained argon by removal of the greatly preponderating nitrogen by means of magnesium (p. 427). The new gas had a molecular weight of about 40, and was therefore more than one-third heavier than nitrogen.

In order to make sure that this substance did not have its source in the magnesium, a different method was used by Lord Rayleigh to separate it from nitrogen. He inclosed the nitrogen with a sufficient quantity of oxygen in a flask, through the sides of which platinum poles had been inserted. A tube entered the flask by the neck, and through this a constant fountain of potassium hydroxide solution played upon the interior and kept the surface covered with fresh quantities of the liquid. Another tube permitted the overflow of the excess of this solution. The discharge of electricity produced nitrogen tetroxide (*q.v.*), which was absorbed by the potassium hydroxide to form potassium nitrate and potassium nitrite. The volume of gas thus continually diminished, and, by persistent sparking of the mixture with oxygen, the nitrogen was finally all taken out. The excess of oxygen was then removed, and the gas which remained was found to be identical with that which Ramsay had obtained.

Lord Rayleigh's method was extremely interesting, since it was a reproduction of an experiment made by Cavendish towards the end of the eighteenth century. The latter had remarked that the assumption that the inert atmospheric gas was a homogeneous single substance had not been confirmed by sufficiently careful experiment. He even endeavored in precisely the above way to remove the nitrogen in order to see whether any other body remained. He records the fact that the residual gas was nothing but a minute bubble, and seems to have dismissed the subject with the idea that if there was any other constituent of the atmosphere present in the nitrogen, its amount was exceedingly small. Argon thus narrowly escaped detection nearly a century before its actual discovery.

The exact density of argon, referred to oxygen = 32, is 39.9. When liquefied it boils at – 186°, and the colorless solid, obtained by cooling the liquid, melts at – 189.5°. The solubility of the gas in water (4 volumes in 100) is two and one-half times that of nitrogen. It has not been found to enter into any sort of chemical combination, and was named argon on this account (Gk. ἄργος, inactive).

Since the atomic weight of a substance is a quantity showing the proportion in which it enters into combination, it will be seen that argon, since it has not yet been found to combine with anything, has, to speak strictly, no atomic weight (pp. 201, 207). At the same time, it is manifestly a question of interest to determine whether the physical properties require the supposition that the molecule of argon contains one atom, or more than one atom.

If gases were composed of perfectly elastic spheres, the molecules

would be altered only in respect to velocity of movement by heating. Calculation enables us to determine that to raise the temperature of one G.M.V. of *such a gas* by one degree would require 3 calories in every case. Now Regnault found the following values (in calories) for the heat capacity of gases:

Oxygen (O_2)	4.96	Carbon dioxide (CO_2)	7.56
Hydrogen (H_2)	4.82	Sulphur dioxide (SO_2),	7.82
Nitrogen (N_2)	4.82	Chloroform ($CHCl_3$)	16.55
Hydrogen chloride (HCl),	4.76	Alcohol (C_2H_6O)	18.70

These gases evidently are not constituted as the hypothesis with which this paragraph opened supposes. Some heat is consumed in work done *inside* the polyatomic molecules, and the amounts by which the numbers exceed 3 calories show that the intramolecular work is greater as the complexity of the molecules increases. Now, in mercury vapor the value is exactly 3, and we have already seen that its atomic and molecular weights are identical (p. 205). According to the molecular hypothesis, its molecules are monatomic, and in them there is no opportunity for the consumption of heat in intramolecular change. Hence, when argon was found likewise to give 3 for the value of its molecular heat-capacity, identity of its atomic and molecular weights was assumed also.

Helium. — In 1868 Lockyer first detected an orange line in the spectrum of the sun's prominences which was not given by any terrestrial substance then known. The line was so conspicuous that it was attributed to the presence, in considerable quantity, of a new chemical element, which was named **helium** (Gk. ἥλιος, the sun). Ramsay, in searching for sources of argon, examined the "nitrogen" which was reported by various mineralogists as being disengaged when certain rare minerals were heated. These minerals, cleveite, uraninite, and bröggerite, were chiefly compounds of uranium, yttrium, and thorium. He was surprised to find (1895) that the gas was not always nitrogen, nor was it even argon. It frequently contained a large proportion of a gas, very much lighter than either, the spectrum of which showed at once that it was identical with helium. The same gas has since been obtained from the water of certain mineral springs, and is found in small amount in the atmosphere. Helium does not exhibit any tendency to enter into combination, either with the elements which its parent minerals contain, or with any others. It is monatomic (*cf.* p. 435); its density shows that its molecular weight is 4. It has not been liquefied by Dewar.

Neon, Krypton, and Xenon. — When the argon obtained from atmospheric nitrogen is cooled with liquid air (−185°), the argon, krypton, and xenon are liquefied, and the neon and helium are dissolved by the liquid. When heat is allowed to reach the mixture, the last two gases escape first, along with much argon. When most of the argon has escaped, the krypton and xenon still remain liquid. By repeated liquefaction and fractional evaporation (see under Petroleum), the krypton and xenon are separated from the argon and from one another. When the vessel containing the mixture of helium and neon is immersed in liquid hydrogen (−240°), the second freezes to a white solid, and the helium, which remains gaseous, can be pumped off.

These gases are all entirely inactive chemically, and are all monatomic. Their molecular weights are: Neon, 20; krypton, 81.5; xenon, 128.

Exercises. — 1. A sample of moist air, confined over water at 15° and 760 mm., occupies 15 c.c. It is mixed with 20 c.c. of hydrogen, and the mixture is exploded, and suffers a contraction of 9.5 c.c. What would be the volume of the oxygen it contained if measured dry at 0° and 760 mm.?

2. Calculate from the data on pp. 427, 428 and the densities the percentage by weight of the three principal components of air.

CHAPTER XXVI

OXIDES AND OXYGEN ACIDS OF NITROGEN

THE names and formulæ of the oxides and oxygen acids of nitrogen are as follows:

Nitrous oxide N_2O	$\longleftarrow$	Hyponitrous acid $H_2N_2O_2$
Nitric oxide NO		
Nitrous anhydride N_2O_3	$\longleftrightarrow$	Nitrous acid HNO_2
Nitrogen tetroxide N_2O_4 and NO_2		
Nitric anhydride N_2O_5	$\longleftrightarrow$	Nitric acid HNO_3.

All the oxides are endothermal compounds, yet, with the exceptions of the third and the last, they are all relatively stable. The acids, when deprived of the elements of water, yield the oxides opposite which they stand. Conversely, excepting in the case of nitrous oxide, the anhydrides with water give the acids. All of these substances are obtained directly or indirectly from nitric acid — nitric anhydride by removal of water, the others by reduction. We turn, therefore, first, to this acid, its sources and properties.

NITRIC ACID.

Sources. — Sodium nitrate, or Chili saltpeter, is found in a desert region near the boundary of Chili and Peru, and chiefly in the former country. The deposit is about 5 feet thick, 2 miles wide, 220 miles in length, and contains 20 to 55 per cent of the salt. Purification is effected by recrystallization. Potassium nitrate, or Bengal saltpeter, is found in the soil in the neighborhood of cities in India, Persia, and other oriental countries. It arises from the oxidation of animal refuse (*cf.* p. 417) through the mediation of nitrifying bacteria. The potash and lime in the soil, along with the product of oxidation of the nitrogen, give nitrates of potassium and calcium. The aqueous extract of this soil is treated with wood ashes, on account of the potash (K_2CO_3) contained in them, is poured off from the calcium carbonate thus precipitated, and is finally evaporated.

The action of the nitrifying bacteria may be imitated in a rough way. Air is caused to pass slowly through concentrated aqueous ammonia, whereby it becomes mixed with ammonia gas. This mixture is led through a wide tube containing platinized asbestos and is then discharged into a large flask. When the asbestos is warmed, it begins to glow, and thereafter the action maintains itself. A part of the ammonia is oxidized to nitric acid, which combines with the excess of ammonia, giving ammonium nitrate. This salt forms a cloud which settles in solid form in the flask.

Preparation. — When any nitrate is treated with any acid, nitric acid is formed by a reversible double decomposition. As sodium nitrate is the cheapest salt of nitric acid, it is always employed. For the same reason, and on account of its activity, and, above all, because of its relative involatility, sulphuric acid is used to displace it:

$$NaNO_3 + H_2SO_4 \leftrightarrows NaHSO_4 + HNO_3\uparrow.$$

The nitric acid is rather volatile (b.-p. 86°), while sulphuric acid (b.-p. 330°) is much less so, and the two salts are not volatile at all. Thus the interaction proceeds to completion very easily (*cf.* p. 259). The materials are heated in cast-iron stills, and the vapor is condensed in earthenware pipes surrounded by water. In many factories a reduced pressure is maintained in the stills and condensers, in order that the distillation may take place at the lowest possible temperature. This precaution is taken to reduce to a minimum the partial decomposition of the nitric acid (see below).

Another action by which attempts are being made to manufacture nitric acid is the direct union of the nitrogen and oxygen of the air under the influence of an electric discharge. The nitrogen tetroxide (NO_2), which is formed in small amounts at a time, is dissolved in water:

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO.$$

The nitric oxide gas, on escaping from the water, unites directly with oxygen to reproduce the tetroxide. The reaction is of interest, independently of this one application, because of its reversibility. It proceeds forward with excess of water, while the reverse action takes place when nitric oxide (*q.v.*) comes in contact with concentrated nitric acid in which the quantity of water is at a minimum.

Physical Properties. — Nitric acid is a colorless, mobile liquid, boiling at 86°, and freezing to a solid which melts at −47°. It fumes

strongly when its vapor issues into moist air (*cf.* p. 282). An aqueous solution containing 68 per cent of the acid boils at 120.5°, while the pure acid, pure water, and all other mixtures, boil at lower temperatures, and have, therefore, higher vapor pressures. On this account a more dilute acid, when heated, loses water until it reaches this strength (*cf.* p. 182). The 68 per cent nitric acid forms the "concentrated nitric acid" of commerce.

Chemical Properties. — 1. Like chloric acid (p. 274), and other oxygen acids of the halogens, nitric acid is most stable when mixed with water. The pure (100 per cent) acid decomposes while being distilled:

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2,$$

yet not with explosive violence like chloric acid. The distillate is colored brown by dissolved nitrogen tetroxide (NO_2). Repeated distillation finally leaves 68 per cent of the acid, mixed with 32 per cent of water formed by the above decomposition. The acid of constant boiling-point is, therefore, reached, as usual, from more concentrated as well as from less concentrated specimens.

"Fuming" nitric acid is brown in color, and contains a considerable amount of dissolved nitrogen tetroxide. It is made by distilling the acid with a little starch. The latter reduces a part of the nitric acid and liberates more of the tetroxide than does mere distillation.

2. Nitric acid combines with small amounts of water to form hydrates HNO_3,H_2O and $HNO_3,3H_2O$, but they are unstable, and are decomposed when more water is added. The formula of the former might be written H_3NO_4, but no salts corresponding to a tribasic acid of this constitution are known (see Phosphoric acid).

3. Nitric acid, when dissolved in water, is highly ionized, and gives a solution containing a relatively large concentration of hydrion. It is therefore active as an acid. By interaction with hydroxides and oxides it forms nitrates.

4. When pure nitric acid (b.-p. 86°) is poured upon phosphoric anhydride, the latter possesses itself of the elements of water, and distillation of the mixture gives nitric anhydride:

$$2HNO_3 + P_2O_5 \rightarrow N_2O_5\uparrow + 2HPO_3.$$

The **anhydride** is a white solid melting at 30° and boiling at 45°. It unites vigorously with water to form nitric acid. It cannot be kept, as

it decomposes into nitrogen tetroxide and oxygen, $2N_2O_5 \rightarrow 4NO_2 + O_2$, with liberation of heat.

5. Like the unstable oxygen acids of the halogens, nitric acid is an oxidizing agent even when diluted with water. The multiplicity of the products into which it may be decomposed by reduction, however, renders separate treatment of this property necessary (see below).

6. Nitric acid interacts energetically with many compounds of carbon. Thus, when heated with phenol (carbolic acid) it gives picric acid, which crystallizes in yellow needles in the mixture :

$$C_6H_5(OH) + 3HONO_2 \rightarrow C_6H_2(OH)(NO_2)_3 + 3H_2O.$$

The presence of water decreases the activity of the molecules. Hence, in this sort of action, which is not ionic, not only is the most concentrated nitric acid employed, but concentrated sulphuric acid is added to assist in the elimination of the water (*cf.* p. 388) that arises as one of the products.

It will be seen that the group NO_2 has taken the place of hydrogen which was formerly attached directly to the carbon of the phenol. Compounds of this kind are called nitro-derivatives. Picric acid is trinitrophenol.

7. Organic compounds of another class, the alcohols (*q.v.*), interact with molecular nitric acid in a different way. The latter is mixed with sulphuric acid with the same object as before. Thus, when glycerine is added slowly to the cooled mixture, glyceryl nitrate (so-called nitroglycerine, see below) is produced :

$$C_3H_5(OH)_3 + 3HONO_2 \rightarrow C_3H_5(ONO_2)_3 + 3H_2O.$$

Here it is the hydrogen of the hydroxyl groups that is displaced by NO_2. The action is not ionic, and the product is not an ionogen. Gun-cotton is made by this action, prepared cotton (cellulose) being employed :

$$(C_6H_{10}O_5)_2 + 6HONO_2 \rightarrow C_{12}H_{14}O_{10}(NO_2)_6 + 6H_2O.$$

8. Nitric acid produces substances of bright-yellow color, known as xanthoproteic acids, when it comes in contact with the skin.

The chemical properties of nitric acid are best represented by the graphic formula :

$$H-O-N\begin{matrix}\nearrow\!\!\!\nearrow O\\ \searrow O\end{matrix}$$

Nitrates. — The nitrates are all more or less easily soluble in water. When heated they decompose (see below). Sodium nitrate is used most largely as a fertilizer. Much is employed in sulphuric acid manufacture, and the rest for conversion into potassium nitrate and in making nitric acid. Potassium nitrate is used, along with sulphur and charcoal, in the manufacture of gunpowder. It furnishes the oxygen with which the charcoal unites; and potassium sulphide, carbon dioxide, and nitrogen are amongst the products of the explosion.

NITRIC OXIDE AND NITROGEN TETROXIDE.

Preparation of Nitric Oxide. — Pure nitric oxide is obtained by adding nitric acid to a boiling solution of ferrous sulphate in dilute sulphuric acid or of ferrous chloride in hydrochloric acid:

$$2FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 \; (+ 2H) \quad \times \mathbf{3} \qquad (1)$$
$$(3H) + HNO_3 \rightarrow NO + 2H_2O \quad \times \mathbf{2} \qquad (2)$$
$$\overline{6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O.}$$

The first partial equation does not take place at all unless an oxidizing agent like nitric acid is present (p. 307). The multiplication of the two partial equations by 3 and 2 respectively is required in order that the hydrogen, which is not a product, may cancel out. This action is used as a means of determining the quantity of nitric acid in a solution, or of nitrates in a mixture, by measurement of the volume of nitric oxide evolved.

As we shall see, this gas may also be obtained when sufficiently dilute nitric acid (sp. gr. 1.2) acts upon copper. Although some nitrous oxide and nitrogen are produced in this interaction, it furnishes a convenient method of generating the gas.

Properties of Nitric Oxide. — Nitric oxide is a colorless gas. In solid form it melts at $-150°$ and the liquid boils at $-142.4°$ under 757.2 mm. pressure. Its solubility in water is slight.

The density of the gas shows the formula to be NO; and there is no tendency to form a polymer, such as N_2O_2, even at low temperatures. This gas is the most stable of the oxides of nitrogen. At 1700° about 0.5 per cent decomposes into nitrogen and oxygen. At 2000° the decomposition reaches 1 per cent. These measurements indicate simply the relative rates at which the resolution into its components occurs, for the action is not reversible, and no equilibrium is established.

Vigorously burning phosphorus continues to burn in the gas, the heat evolved liberating the oxygen required for the continuation of the combustion. Burning sulphur and an ignited taper, however, are extinguished.

Nitric oxide has two characteristic properties. It unites directly with oxygen in the cold to form the reddish-brown nitrogen tetroxide :

$$2NO + O_2 \rightleftarrows 2NO_2.$$

The same result follows when it is led into warm concentrated nitric acid (*cf.* p. 439) :

$$NO + 2HNO_3 \rightleftarrows 3NO_2 + H_2O.$$

It also unites with a number of salts, the compound in the case of ferrous sulphate being capable of existence in solution and possessing a brown color. The composition of this compound (a molecular compound, see below) has not been determined, but at 8° the proportion of nitric oxide absorbed by the solution is about $2NO : 3FeSO_4$.

Since ferrous sulphate will first reduce nitric acid to nitric oxide (p. 442), and the excess of the salt will then give a brown color with the product, a delicate test for nitric acid is founded upon the above action. The substance supposed to contain a nitrate is mixed with a strong solution of ferrous sulphate, and concentrated sulphuric acid is poured down the side of the tube so as to lie below the lighter mixture (Fig. 89). At the surface of contact the sulphuric acid liberates the nitric acid, and a brown layer is seen. Even when the amount of the nitrate is very small, the brown tint may be distinctly made out by contrast with the nearly colorless liquids above and below it.

FIG. 89.

Molecular Compounds. — When substances formed by union of two compounds have a prevailing tendency to decompose into the same two materials, and exhibit the chemical properties of their constituents rather than individual ones of their own, they are often called **molecular compounds**. Thus the above substance, $3FeSO_4$, 2NO, gives off the nitric oxide again when warmed, and its solution has the properties of a mixture of ferrous sulphate and nitric oxide. Similarly, hydrates (pp. 120, 123) are formed by union of salts or other substances with water, and are apparently, for the most part, decom-

posed by solution. Double salts (p. 360), such as **ferrous-ammonium sulphate** $FeSO_4,(NH_4)_2SO_4, 6H_2O$, of which very many are known, are of the same character. They are stable only in the solid form. There are also compounds of salts with ammonia (see Compounds of copper and silver), and with carbon monoxide (CO), one such compound being formed with cuprous chloride (*q.v.*).

The name *molecular compounds* is derived from the supposition that, in these compounds, the molecules of the components retain their integrity to some extent and are thus ready to be liberated. This is an attempt to explain the fact that the behavior is that of the constituents. It distinguishes molecular compounds from substances like ammonium chloride and phosphorus pentachloride. The former may be made by union of HCl and NH_3, but usually behaves rather as if composed of NH_4 and Cl. The latter (*q.v.*) dissociates into PCl_3 and Cl_2, but with water gives phosphoric acid (*cf.* p. 181), which is derivable from the pentachloride only. The distinction is of practical rather than theoretical importance, however, for there are all gradations in the behavior of molecular compounds. It is useful simply as a rough means of classifying and remembering certain facts.

Distinguishing molecular compounds from ordinary compounds is further justified by the fact that the constituents of molecular compounds often seem to be saturated (p. 379), and no ordinary valences are available for holding the new material. Thus in $Ca^{II}Cl_2^{I}$ the ordinary valences are all saturated. Yet the salt forms the hydrate $CaCl_2,6H_2O$ with water ($H_2^{I}O^{II}$) which is likewise a saturated compound. The conception of molecular compounds implies, therefore, the idea of a sort of *valence of molecules*. Thus $FeSO_4$ forms $FeSO_4,7H_2O$ and $FeSO_4,(NH_4)_2SO_4,6H_2O$, and $FeSO_4,K_2SO_4,6H_2O$, in all of which *seven* other molecules are combined with it. The sulphates of other bivalent metals (*q.v.*), such as copper and magnesium, form molecular compounds of the same nature. Ammonium chloride, on the other hand, is not a molecular compound, because, although NH_3 unites with HCl, HBr, HI, and HF, yet nitrogen is quinquivalent, and substances like N_2O_5, NH_4Cl, etc., may fitly be regarded as ordinary compounds.

Preparation of Nitrogen Tetroxide. — This substance is liberated by heating nitrates, other than those of potassium, sodium, or ammonium:

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2.$$

In most cases the oxide of the metal remains. When the mixed gases are led through a U-tube immersed in a freezing mixture, the tetroxide condenses as a pale-yellow liquid, and the oxygen passes on.

The compound may also be made by direct union of nitric oxide and oxygen, or by oxidation of nitric oxide by concentrated nitric acid (p. 443). It is likewise almost the sole product of the interaction of concentrated nitric acid and copper (see below). If any nitric oxide were produced by the primary action, it would be oxidized to nitrogen tetroxide in passing up through the acid.

Properties of Nitrogen Tetroxide.—The most striking peculiarity of this gas is that, when hot, it is deep brown in color, and when cold, pale yellow. When cooled, it gives a pale-yellow liquid boiling at 22°, and an almost colorless solid melting at about −12°. The density of the vapor decreases very rapidly from 27° to 140°, and increases again as the temperature falls. The molecular weights calculated from these observations are: at 27°, 76.7; at 70°, 55.6; at 135°, 46.3; at 154°, 45.7. Now the molecular weights corresponding to the formulæ N_2O_4 and NO_2 are 92 and 46 respectively, so that these results mean that the deep-brown gas is NO_2, and that as this is cooled it combines to form the colorless N_2O_4. Measurement of the depression the substance causes in the freezing-point (*cf.* p. 291) of glacial acetic acid gives the molecular weight 92, so that in solution and at the temperature of freezing acetic acid (below 17°) the substance is all N_2O_4.

When the temperature is carried above 154°, by passing the brown gas through a red-hot tube, the brown color disappears once more, and nitric oxide and oxygen are formed. On cooling, the same steps through brown gas to pale-yellow gas are retraced:

$$\underset{\text{Colorless}}{2NO + O_2} \rightleftarrows \underset{\text{Brown}}{2NO_2} \rightleftarrows \underset{\text{Colorless.}}{N_2O_4},$$

Since nitrogen tetroxide yields free oxygen more readily than does nitric oxide, most ordinary combustibles burn in it. It has powerful oxidizing properties; and "fuming nitric acid," which contains it in solution, is employed when oxidation is the special object in view.

This oxide is intermediate in composition between nitrous and nitric anhydrides, and, when dissolved in *cold* water, gives both nitric and nitrous acids:

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2.$$

If a base is present, a mixture of the nitrate and nitrite of the metal is produced (*cf.* p. 275).

When the water is not cooled, the nitrous acid (*q.v.*), being unstable, gives nitric oxide and nitric acid, so that the result is:

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO.$$

OXIDIZING ACTIONS OF NITRIC ACID.

When nitric acid gives up oxygen to any body, it is itself reduced. Hence, according to convenience, we shall refer to oxidations by, or reductions of nitric acid.

Nascent Hydrogen. — The extent to which the acid is reduced by nascent hydrogen depends on the particular metal with which the hydrogen is in contact when liberated (*cf.* p. 424). Thus, with zinc and very dilute nitric acid, almost the only product, aside from zinc nitrate, is ammonia:

$$4Zn + 8HNO_3 \rightarrow 4Zn(NO_3)_2 (+ 8H) \quad (1)$$
$$(8H) + HNO_3 \rightarrow NH_3 + 3H_2O \quad (2)$$
$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \quad (3)$$
$$\overline{4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O}$$

With the excess of nitric acid, ammonium nitrate is formed. Again, when tin is the metal, the reduction is less complete, and hydroxylamine is a product (p. 423).

When metals more active than zinc, such as magnesium, are used, some of the hydrogen escapes oxidation and is liberated.

Heavy Metals. — Metals less active than tin, such as copper and silver, do not displace hydrogen from dilute acids (p. 362), but reduce nitric acid, nevertheless, and are converted into nitrates. Platinum and gold (*cf.* p. 389) alone are not attacked. Thus, copper, with somewhat *diluted* nitric acid, gives cupric nitrate and nitric oxide (NO). In making the equation for this action we may resolve the formula of nitric acid into those of water and the anhydride H_2O,N_2O_5. This shows that the two molecules of the acid will give 2NO, and 3O will remain:

$$2HNO_3 \rightarrow H_2O + 2NO (+ 3O) \quad (1)$$
$$(3O) + 6HNO_3 + 3Cu \rightarrow 3H_2O + 3Cu(NO_3)_2 \quad (2)$$
$$\overline{8HNO_3 + 3Cu \rightarrow 4H_2O + 2NO + 3Cu(NO_3)_2}$$

The nitric oxide is liberated as a colorless gas, but forms the brown tetroxide at once on meeting the oxygen of the air (p. 443).

When *concentrated* nitric acid is used with copper, almost pure nitrogen tetroxide is obtained:

$$2HNO_3 \rightarrow H_2O + 2NO_2\ (+O) \qquad (1)$$
$$(O) + 2HNO_3 + Cu \rightarrow H_2O + Cu\,(NO_3)_2 \qquad (2)$$
$$\overline{4HNO_3 + Cu \rightarrow 2H_2O + 2NO_2 + Cu(NO_3)_2}$$

The equations for actions like the above may be built up from partial equations of various kinds (*cf.* p. 229). Thus we may begin by forming the nitrate of the metal, and then use the balance, consisting of hydrogen, along with other molecules of nitric acid to secure the oxide and water:

$$Cu + 2HNO_3 \rightarrow Cu(NO_3)_2(+2H)$$
$$(2H) + 2HNO_3 \rightarrow 2H_2O + 2NO_2$$
$$\overline{Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2}$$

As the subdivision is purely arithmetical (p. 229), this procedure does not involve the assumption that copper does actually displace hydrogen as a free element. Yet it would not necessarily be incorrect to make even this supposition. Although unable to liberate hydrogen in quantity from a dilute acid, copper may be held, if we choose, to displace a minute amount of it:

$$Cu + 2HNO_3 \leftrightarrows Cu(NO_3)_2 + H_2, \quad \text{or} \quad Cu + 2H^{\cdot} \leftrightarrows Cu^{\cdot\cdot} + H_2,$$

and to be restrained by the much more vigorous reverse action (p. 362) from continuing this operation. In this point of view the oxidation of the trace of free hydrogen by the excess of nitric acid continuously annihilates the possibility of reverse action.

Complexities of Oxidation by Nitric Acid. — The above are types of the interactions of metals with nitric acid. In actual experiments the behavior is usually more complex. Thus, as a rule, the action is very slow at first, and gathers speed with the accumulation of the reduction products, which act catalytically.

Again, different concentrations of nitric acid give different products with the same metal. The most conspicuous effect of this kind is the production of nitric oxide with diluted acid, and the invariable formation of nitrogen tetroxide with concentrated acid. This is explained by the fact that nitrogen tetroxide cannot pass unchanged through a liquid containing much water, for it gives nitric acid and nitric oxide with the latter (p. 439). Conversely, where the nitric acid is concentrated, nitric oxide, even if formed by the interaction with the metal, must be oxidized to nitrogen tetroxide as it passes up through the liquid (p. 443).

Finally, intermediate concentrations give mixtures of these two oxides, and, with zinc, even nitrous oxide (N_2O) and nitrogen may be found in considerable quantities in the gases evolved.

Non-Metals. — With non-metals the actions are different in so far that these elements do not give nitrates. Thus, sulphur boiled in nitric acid gives sulphuric acid, along with nitric oxide, equation (3), or with nitrogen tetroxide, equation (6), or with both, according to the concentration of the acid:

$$2HNO_3 \rightarrow 2NO + H_2O\ (+\ 3O) \quad (1)$$
$$(3O) + H_2O + S \rightarrow H_2SO_4 \quad (2)$$
$$2HNO_3 + S \rightarrow 2NO + H_2SO_4 \quad (3)$$

$$2HNO_3 \rightarrow 2NO_2 + H_2O + O \quad \times 3 \quad (4)$$
$$(3O) + H_2O + S \rightarrow H_2SO_4 \quad (5)$$
$$6HNO_3 + S \rightarrow 6NO_2 + 2H_2O + H_2SO_4 \quad (6)$$

The reader will note (*cf.* p. 272) that a separate equation, (3) and (6), must be made for the formation of *each* reduction product. If NO and NO_2 are both formed, they cannot arise from the same molecule of nitric acid. They result from two actions which are independent, although proceeding simultaneously in the same vessel (*cf.* p. 231). Thus the equation:

$$2HNO_3 + C \rightarrow H_2O + CO_2 + NO + NO_2,$$

is a misrepresentation. It implies that equimolar quantities of the two oxides of nitrogen are formed. But this could only occur by chance, and the balance would be destroyed the next moment by the lowering in the concentration of the acid, giving the advantage to the nitric oxide.

Compounds. — Compounds like hydrogen sulphide, hydrogen iodide, and sulphurous acid, which are easily oxidized, interact with nitric acid. With diluted nitric acid the products are free sulphur, iodine, and sulphuric acid respectively.

The mixture of nitric acid and hydrochloric acid is known as *aqua regia.* The chlorine set free by the oxidation of the hydrochloric acid is more active than is the ordinary solution of chlorine in water, perhaps in consequence of catalytic action of the substances in this solution, and combines with gold and platinum (*q.v.*), converting them into chlorides. Nitrosyl chloride (NOCl), which, however, does

not interact directly with the noble metals, is formed at the same time:

$$Cl-H+H-O-\overset{\overset{O}{\|}}{N}=O+2H\,Cl \rightarrow 2H_2O + Cl_2 + Cl-N=O.$$

The interaction with platinum is, therefore:

$$8HCl + 2HNO_3 + Pt \rightarrow H_2PtCl_6 + 2NOCl + 4H_2O.$$

Chlorine, in this active state of the element, may be spoken of as nascent chlorine (*cf.* p. 423).

Nitrous Acid, Hyponitrous Acid, and their Anhydrides.

Nitrites. — When the nitrates of potassium and sodium are heated, they lose one unit of oxygen, and the nitrites remain:

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2.$$

Commonly lead is stirred with the melted nitrate and assists in the removal of the oxygen. The litharge (PbO) which is formed remains as a residue when the sodium nitrite is dissolved for recrystallization.

Nitrous Acid. — When an acid is added to a dilute solution of a nitrite, a pale-blue solution containing nitrous acid is obtained. The acid is very unstable, however, and, when the solution is warmed, it decomposes:

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O.$$

When a concentrated solution of sodium nitrite is acidified, the nitrous acid decomposes at once, and a brown gas containing the anhydride escapes:

$$2H^{\cdot} + 2NO_2{}' \leftrightarrows 2HNO_2 \leftrightarrows H_2O + N_2O_3 \uparrow.$$

This behavior distinguishes a nitrite from a nitrate.

Reducing agents deprive nitrous acid of part or all of its oxygen:

$$2HI + 2HNO_2 \rightarrow 2H_2O + 2NO + I_2.$$

Indigo is also converted by it into isatine (*cf.* p. 269). On the other hand, oxidizing agents which are sufficiently active, like acidified potassium permanganate, convert nitrous acid into nitric acid:

$$3H_2SO_4 + 2KMnO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O\ (+\ 5O) \qquad (1)$$
$$(5O) + 5HNO_2 \rightarrow 5HNO_3 \qquad (2)$$
$$\overline{3H_2SO_4 + 2KMnO_4 + 5HNO_2 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5HNO_3}$$

Nitrous acid is much used in the making of organic dyes.

Nitrous Anhydride. — A study of the gas arising from the decomposition of nitrous acid shows that in the gaseous state the anhydride is almost entirely dissociated:

$$N_2O_3 \rightleftarrows NO + NO_2.$$

When the mixture is led through a U-tube immersed in a freezing mixture at $-21°$, a deep-blue liquid is obtained which appears to be the anhydride itself. This begins to dissociate before reaching its boiling-point, and at $+2°$ gives off nitric oxide.

The same equimolar mixture of the two gases is obtained by the action of water on nitrosylsulphuric acid (p. 383).

Hyponitrous Acid. — This acid is formed by the interaction of hydroxylamine and nitrous acid in aqueous solution:

$$H-O-N\boxed{H_2+O}N-O-H \rightarrow H_2O + H-O-N=N-O-H.$$

With nitrate of silver, the yellow, insoluble silver hyponitrite $Ag_2N_2O_2$ is precipitated. When this salt is shaken with an ethereal solution of hydrogen chloride, the acid is liberated, and the insoluble silver chloride may be separated by filtration. Finally, evaporation of the ethereal solution leaves hyponitrous acid as a white mass. It explodes when heated, and its solution in water is an exceedingly feeble acid. The warm aqueous solution decomposes slowly, giving nitrous oxide:

$$H_2N_2O_2 \rightarrow H_2O + N_2O,$$

and this change is not capable of reversal.

Nitrous Oxide. — Nitrous oxide is prepared by heating ammonium nitrate, or a mixture of a salt of ammonium and a nitrate:

$$NH_4NO_3 \rightarrow 2H_2O + N_2O.$$

The steam condenses, and the nitrous oxide may be collected over warm water, or dried and compressed into steel cylinders.

Its solubility in cold water is considerable: 130 volumes in 100 at

0°. At 25° this falls to 60 volumes in 100. In dissolving, the gas forms no compound with water. The substance melts at – 102.3°, and boils at – 89.8°. The vapor tension of the liquid at 0° is 30.75 atmospheres; at 12°, 41.2 atmospheres; and at 20°, 49.4 atmospheres. The critical temperature is 38.8°.

A glowing splinter of wood bursts into flame when introduced into nitrous oxide, and phosphorus, sulphur, and other combustibles, burn in it with much the same vigor as in oxygen. In all cases oxides are formed, and nitrogen is set free. The rapidity with which bodies combine with oxygen obtained from nitrous oxide is doubtless due to the fact that it is an endothermal compound, and the heat liberated by its decomposition assists the ensuing combustion:

$$2N_2O \rightarrow 2N_2 + O_2 + 2 \times 18{,}000 \text{ cal.}$$

It is to be noted that the effect of the heat of decomposition will be partly offset by the dilution of the oxygen with nitrogen. Yet the proportion of nitrogen to oxygen is only half as great as in air, so that on the whole the conditions are much more favorable to combustion in this gas.

Nitrous oxide, when cold, does not behave like free oxygen. Nitric oxide, when mixed with it, gives none of the red nitrogen tetroxide. Metals do not rust in it, and the hæmoglobin of the blood is unable to use it as a source of oxygen. It was Davy who first observed that nitrous oxide could be taken into the lungs, and that, since it furnished no oxygen, insensibility followed its use. By suitable admixture of an amount of air sufficient to sustain life, it is employed as an anæsthetic for minor operations. The hysterical symptoms which were observed to accompany its administration, and caused it to receive the name of "laughing gas," are such as attend the use of all anæsthetics.

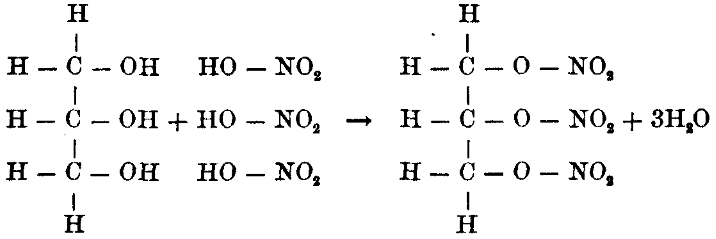
Graphic Formulæ of Nitric Acid and its Derivatives: Explosives. — The following equation shows the graphic formulæ of nitric acid and of ammonium nitrate:

$$\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\rangle \mathrm{N{-}OH} + \mathrm{H{-}O{-}N}\begin{matrix}\nearrow \mathrm{O}\\ \searrow \mathrm{O}\end{matrix} \rightarrow \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\rangle \mathrm{N{-}O{-}N}\begin{matrix}\nearrow \mathrm{O}\\ \searrow \mathrm{O}\end{matrix} + H_2O.$$

The structural formula of the latter is intended to explain the fact that the salt is able to exist at all, by representing the oxygen and hydrogen as being separated from one another and attached to differ-

ent nitrogen units. When the equilibrium of the system is disturbed by heating, the oxygen and hydrogen unite to form water, an arrangement which is much more stable, and nitrous oxide (see above) escapes with the steam.

The decomposition of nitroglycerine and gun-cotton (p. 441), as well as of ammonium nitrite (p. 416), is explained in the same way. These substances are made by actions which, like the above neutralization, take place in the cold, and the groups, containing the oxygen on the one hand and carbon and hydrogen on the other, become quietly united without more serious interaction. Thus the formation of nitroglycerine (p. 441) appears as follows:



When the nitroglycerine is heated, or receives a mechanical shock, the oxygen all unites with the carbon and hydrogen, and the nitrogen escapes:

$$4C_3H_5(ONO_2)_3 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2.$$

That nitroglycerine is a more sensitive explosive than gunpowder is due to the fact that, in the former, the materials required for the chemical change are already within the same molecule, whereas in the latter (*q.v.*) they are contained in the separate molecules of a mixture. Even after the most careful incorporation, the oxygen of the potassium nitrate can hardly be uniformly so near to the carbon mechanically mixed with the salt, as are these elements in nitroglycerine or gun-cotton. In the latter the oxidation of the hydrogen and carbon is intramolecular.

Substances like hydrazoic acid (p. 422) and nitrogen iodide (p. 425) might seem to constitute a third kind of explosive. Here the change consists in the resolution of the compound into its constituents. Still, if we consider the case of hydrazoic acid, for example: $2N_3H \rightarrow 3N_2 + H_2$, we see that the action consists, after all, in the union of the constituents to form the more stable combinations N_2 and H_2. It is, therefore, similar in principle to the explosion of nitroglycerine.

The Principle of Transformation by Steps. — It may have occurred to the reader as strange that it should be possible to make nitric anhydride by distilling a warm mixture (p. 440) when the product decomposes spontaneously, even when kept in the cold. How can a compound be fitted together under certain conditions, when under the same or, even, under more favorable conditions it proves to be incapable of continued existence? We should expect rather that obtaining the products of its decomposition would have been the only result of the effort to make it.

Extraordinary as this fact appears to be, it is nevertheless very commonly encountered. Perchloric acid is made by a distillation (p. 276) and afterwards breaks up of its own accord. So, also, hypochlorites are formed first and can be isolated. But under the same conditions the further transformation to chlorates will occur (p. 272). A simple case is that of sulphur made by precipitation (p. 376) at the ordinary temperature. Although it is naturally solid below 119°, yet, when first thrown down, it is in the form of liquid droplets which, if undisturbed, may remain fluid for weeks. Similarly, sulphur vapor condenses on glass in drops which remain liquid until they are touched or rubbed. Finally, a supersaturated solution (p. 159) is not unlike cold liquid sulphur.

In all these cases there is a possibility of further change, which, when it comes, will liberate heat or some other form of energy. Thus, heat is set free when the liquid sulphur is precipitated. The amount of heat would have been greater, by the heat of fusion of the sulphur, if solidification had occurred simultaneously. But, in spite of the existence of this justification for the final step, this step is not taken. So, the decomposition of the vapor of the perchloric acid or of the nitric anhydride would have added to the amount of energy liberated as heat, but this additional step was postponed. In other words, **transformations which proceed spontaneously** and with evolution of heat **may go forward by steps, when there are intermediate substances capable of existence.** This is known as the **principle of transformation by steps**, and was first described by Ostwald.

Exercises. — 1. Make the equation for the interaction of ferrous chloride, hydrochloric acid, and nitric acid (p. 442), and for all the actions concerned when the test for a nitrate (p. 443) is applied to sodium nitrate. What volume (at 0° and 760 mm.) of NO is obtained from one formula-weight of nitric acid (p. 216, Ex. 8)?

2. Should you classify as molecular compounds (p. 443): Chlorine hydrate, ammonium hydroxide, KI_3 (p. 235), sulphurous acid, sodium pentasulphide (p. 376)? Justify your answer.

3. At 27°, what proportions of the molecules of nitrogen tetroxide are in the forms of NO_2 and N_2O_4 respectively (p. 445)? At the same temperature what fraction of the material, by weight, is in the former condition? What are the relative volumes of the tetroxide, and of the nitric oxide and oxygen obtained by its decomposition (p. 445)?

4. Make an equation showing the production of nitrous oxide by the action of zinc on nitric acid.

5. Make the correct equations showing the formation of nitric oxide and nitrogen tetroxide by the interaction of carbon and nitric acid (p. 448).

6. Justify the graphic formula assigned to nitric acid (p. 441).

7. Using the anhydride method (p. 274), make the equations for the interactions of N_2O_4 and water (p. 445) and of nitric acid and sulphur (p. 448).

8. Make a classified list, with examples, of all the kinds of interactions which, in this and preceding chapters, have been named oxidations and reductions (*e.g.* pp. 70, 72, 110, 170, 172, 231, 237, 269, 306, 374, 420, 424, 446. See also Chemistry of copper and tin).

CHAPTER XXVII

PHOSPHORUS

The Chemical Relations of the Element. — There are many things in the chemistry of phosphorus and its compounds which remind us of nitrogen. Yet these are largely referable to the fact that the elements are both non-metals and both have the same valences, viz. three and five. The behavior of the compounds is often very different. For the present it is sufficient to say that both give compounds with hydrogen, NH_3 and PH_3, and both yield oxides of the forms X_2O_3, X_2O_4, and X_2O_5. The first and last of these oxides are acid-forming, and phosphorus, therefore, gives acids corresponding to nitrous and nitric acids, although there is more variety in the proportion of water combined with the anhydride (*cf.* p. 278). The element is thus a non-metal (see Comparison with nitrogen and with sulphur, end of this chapter).

Occurrence. — This element is found widely disseminated in nature, usually in the form of phosphates. Calcium phosphate, for example, which is derived (p. 278) from phosphoric acid (H_3PO_4) by displacement of its hydrogen by calcium, and has, therefore, the formula $Ca_3(PO_4)_2$, is found in most soils. It constitutes a large part of the solid material of the bones and teeth of animals and of the beds of fossil bones found in Florida and Tunis. A conspicuous mineral related to this substance is apatite, $Ca_5F(PO_4)_3$. It is found in large quantities in Canada, and is a component of many rocks. Complex organic compounds containing phosphorus are essential constituents of protoplasm and of the materials of the nerves and the brain.

Preparation. — Brand, merchant and alchemist, of Hamburg, discovered phosphorus (1669) by distilling the residue from evaporated urine, in the course of his search for the Philosopher's stone. The mode of preparing it from bone-ash was first published by Scheele (1771). Green bones contain about 58 per cent of calcium phosphate. After the gelatine has been extracted from them, by means of water boiling under pressure, they are subjected to destructive distillation, a

process which yields bone-oil. The residue is a mixture of carbon (*q.v.*) and calcium phosphate. It is used by sugar refiners as a decolorizer. When its powers in this direction have been exhausted, it is **calcined** — that is to say, all the combustible matter is burned out of it, — and the product is bone-ash. Formerly this was used in making phosphorus, but now the less expensive calcium phosphate of fossil origin is employed.

A mixture of powdered bone-ash or calcium phosphate and sulphuric acid (sp. gr. 1.5 to 1.6) is heated with steam and stirred in a wooden vat:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4.$$

The calcium sulphate is partly precipitated during the heating. The liquid obtained by filtration is evaporated in leaden pans. During this process most of the remainder of the calcium sulphate is deposited and a syrupy, crude phosphoric acid is obtained. This acid is mixed with sawdust, or carbon in some form, and the mixture is first heated to a moderate temperature and then distilled in earthenware retorts. Two actions take place in succession. The phosphoric acid loses water and turns into metaphosphoric acid, then the latter is reduced by the carbon, carbon monoxide and phosphorus vapor passing off:

$$H_3PO_4 \rightarrow H_2O + HPO_3,$$
$$2HPO_3 + 6C \rightarrow H_2 + 6CO + 2P.$$

A white heat is required for the distillation, and a pipe from the tubular clay retort conducts the vapors into cold water, in which the phosphorus collects.

A much simpler process depends on the use of the electric furnace (Fig. 90). The calcium phosphate is mixed with the proper proportions of carbon and silicon dioxide (sand), and the mixture is introduced continuously into the furnace. The discharge of an alternating current between carbon poles produces the very high temperature which the action requires. The calcium silicate which is formed fuses to a slag, and can be withdrawn at intervals. The gaseous products pass off through a pipe and the phosphorus is caught under water:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 5CO + 2P.$$

We may regard the phosphate as being composed of two oxides, $3CaO, P_2O_5$. It thus appears that the calcium oxide has united with the

silica, which is an acid anhydride (*cf.* p. 381) : $CaO + SiO_2 \rightarrow CaSiO_3$, while the phosphoric anhydride has been reduced.

The phosphorus, after purification, is cast into sticks in tubes of tin or glass, standing in cold water.

The Electric Furnace. — By an electric furnace is understood an **electro-thermal** arrangement in which the heat produced by some resistance offered to the current, such as that of an air-gap between the carbons, is used to produce chemical change. Electrolysis plays no part in the phenomena, and an alternating current, which can produce no electrolytic decomposition, is generally employed. The restricted area within which the heat is developed makes possible the attainment of a high temperature (see Calcium carbide).

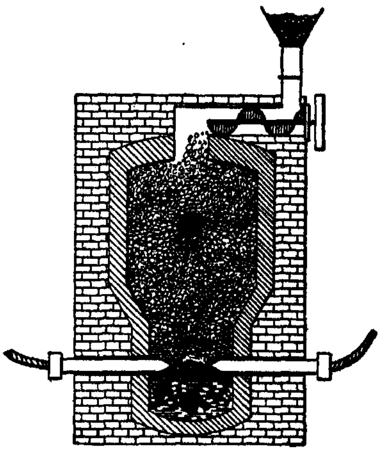


FIG. 90.

Physical Properties. — There are two perfectly distinct kinds of phosphorus, known as ordinary, or yellow phosphorus, and red phosphorus. **Yellow phosphorus**, prepared as described above, is at first transparent and colorless, but after exposure to light acquires a superficial coating of the red variety. It melts at 44° and boils at 269° (according to some authorities, at 287°). Its molecular weight is, at 313°, 128, and at a red heat 119.8. As the atomic weight is 31, the formula, within this range, is P_4. At 1700° the value 91.2 is held to indicate partial dissociation into P_2. In solution the formula is P_4. Yellow phosphorus is very soluble in carbon disulphide, less soluble in ether and other organic solvents, and insoluble in water. It is exceedingly poisonous, less than 0.15 g. being a fatal dose. Continued exposure to its vapor causes necrosis, a disease from which matchmakers are liable to suffer. The jawbones and teeth are particularly liable to attack.

Red phosphorus is a dull red powder consisting of small tabular crystals. It is obtained by heating yellow phosphorus to about 250° in a vessel from which air is excluded. The change is much more

rapid at slightly higher temperatures. Since a great amount of heat is evolved in the transformation, the action is apt to become violent and to cause volatilization of a large part of the phosphorus. In presence of a trace of iodine the transformation is greatly accelerated, and takes place even in the cold.

Red phosphorus does not melt, but passes directly into vapor. Its vapor is identical with that of yellow phosphorus. It is insoluble in carbon bisulphide and other solvents. It is not poisonous, and, unlike yellow phosphorus, does not require to be kept under water to avoid spontaneous combustion.

Chemical Properties. — Yellow phosphorus unites directly with the halogens with great vigor. It unites slowly with oxygen in the cold, and with sulphur and many metals when the materials are heated together.

The slow union of phosphorus with atmospheric oxygen is accompanied by the evolution of light, although the temperature is not such as we usually associate with incandescence. The name of the element (Gk. φῶς, light; φέρω, to bear) records this property. Apparently the chemical energy, transformed in connection with the oxidation, is converted, in part at least, into radiant energy instead of completely into heat.* A curious fact in connection with the luminosity and concomitant oxidation of phosphorus is that these occurrences depend upon the concentration of the oxygen gas as well as upon the temperature. Thus, phosphorus does not shine or oxidize in pure oxygen below 27°. If the concentration of the oxygen is reduced to 200 mm. or less by means of a pump, or by mixing with an indifferent gas such as nitrogen, phosphorescence becomes perceptible at the ordinary temperature. This explains the luminosity shown in the air. At lower temperatures, lower pressures have to be used. The phosphorescence may be destroyed by the vapor of turpentine and other substances, which perhaps act as catalytic agents and restrain the oxidation.

* The same production of light from chemical action in a cold body is seen in the luminosity of certain parts of some animals, such as fireflies and some species of fish. In many violent chemical changes the light given out is conspicuously greater than that proper to the temperature produced (*cf.* p. 73), and must come, therefore, in part, directly from the chemical energy. Thus, burning magnesium has a temperature of about 1350°, while the production of light of the same character, by mere incandescence, would require a temperature of about 5000°.

The difference in behavior of pure and diluted oxygen may be shown by pouring a solution of phosphorus in carbon disulphide on to two strips of filter paper. One of the strips, hung in the air, catches fire as soon as the evaporation of the solvent has exposed a large area of finely divided phosphorus. The other, hung in a jar of oxygen, remains unaffected, but becomes ignited instantly upon removal from the jar.

The slow oxidation of phosphorus is accompanied by the production of ozone, but the nature of the action is still unknown.

Chemical Properties of Red Phosphorus.—This variety of the element, since it is formed with evolution of heat, contains less energy than yellow phosphorus and is much less active. It does not catch fire in the air below 240°, while ordinary phosphorus ignites at 35–45°. Indeed, it is the vapor that begins to combine with oxygen, and this behavior is only an independent proof of the low vapor tension of the red variety. When the vapor tension of yellow phosphorus has reached 760 mm. (at 269°, the b.-p.), that of red phosphorus is almost imperceptible. Even when the former has become two atmospheres, the latter is still very small.

Red phosphorus is to be regarded as the normal, stable form of phosphorus. The fact that yellow phosphorus can be kept a great length of time, and is changed but slightly on exposure to light, only shows that the transformation into a stabler condition is retarded by the lowness of the temperature (*cf.* p. 72). The relation between the two varieties of phosphorus is quite distinct from that between rhombic and monoclinic sulphur (p. 368). In the latter case there is a definite temperature of transformation (96°) above which one form completely disappears, and below which the other form is incapable of permanent existence. With the varieties of phosphorus no such point of transformation exists. The red phosphorus is the more stable at all temperatures at which both forms are known. The yellow turns into red, but the red never into the yellow. It is only by condensing the vapor that the yellow kind is obtained. It seems probable that red phosphorus is a polymer (p. 242) of yellow phosphorus (P_4). The production from the vapor (also P_4) of the yellow solid, instead of the red solid whose formation would be accompanied by a larger liberation of heat, is simply an illustration of the principle of transformation by steps (p. 453).

When two or more forms of an element, or even of a compound (see Isomers), occur, they are commonly spoken of as **allotropic modifications**. The term is applied to oxygen and ozone (*q.v.*) which are certainly, and to red and yellow

phosphorus which are, probably, chemically distinct substances. It is used also of rhombic and monoclinic sulphur, where the difference is purely physical. In short, it has at present no scientific value, for it covers a heterogeneous mass of phenomena which, in part, still await elucidation. If **allotropic modifications** were to be defined as **substances** (p. 32) **composed of the same materials, but possessing different proportions of free or available energy**, and, therefore, different physical properties and different degrees of chemical activity, which is apparently the sense in which the expression is commonly employed, then ice, water, and steam would be examples of such substances. In each of the above four illustrations, the second (in the case of water, the third) is the more active form.

Uses of Phosphorus. — The greater part of the phosphorus of commerce is employed in the manufacture of matches. The first articles of this sort (1812) were sticks coated with sulphur and tipped with a mixture of potassium chlorate and sugar. For ignition they were dipped into a bottle containing asbestos moistened with concentrated sulphuric acid. Matches involving the use of phosphorus (1827) have now displaced all others. In making common matches which strike on any rough surface, the sticks are first dipped in melted sulphur or paraffin to the extent of about half an inch. The head is often composed of manganese dioxide or red lead, and a little potassium chlorate, which supply oxygen, a small proportion of free phosphorus and antimony trisulphide, which are both combustible, and dextrine or glue. A paste made of these materials is spread evenly upon a slab, and the prepared sticks fixed in a frame are dipped once or twice in the mixture.

In the case of "safety" matches, the mixture upon the head is not easily ignited by itself. It is composed of potassium chlorate or dichromate, some sulphur or antimony trisulphide, and a little powdered glass to increase the friction, all held together with glue. Upon the rubbing surface on the box is a thin layer of antimony trisulphide mixed with red phosphorus and glue. The friction converts a little of the red phosphorus into vapor. To prevent smoldering of the burned matches, the upper ends of the sticks are sometimes soaked in a solution of alum or sodium phosphate.

A small amount of yellow phosphorus is employed in making rat poison, which is a mixture of phosphorus, lard (as solvent), and flour, made into dough.

Phosphine. — Three hydrides of phosphorus are known. These are, phosphine PH_3 (a gas), a liquid hydride P_2H_4, which is presumably

the analogue of hydrazine (N_2H_4), and a solid hydride P_4H_2. **Phosphine** does not seem to be produced under ordinary circumstances by the direct union of the elements. It is formed slowly, however, by the action of nascent hydrogen, from zinc and hydrochloric acid at 70°, upon yellow phosphorus. The gas may be made by boiling yellow phosphorus with potassium hydroxide solution in an apparatus similar to that used for generating hydrogen. Potassium hypophosphite is formed at the same time:

$$3KOH + 4P + 3H_2O \rightarrow 3KH_2PO_2 + PH_3.$$

The gas made in this fashion contains a small proportion of the vapor of the liquid hydride, which is spontaneously inflammable, and consequently the mixture catches fire on emerging into the air from the delivery tube. To avoid explosions, the air in the flask must be displaced by hydrogen or illuminating-gas before heat is applied. This product contains also free hydrogen, in increasing quantities as the action goes on, in consequence of the reduction of the water and potassium hydroxide by the potassium hypophosphite: $KH_2PO_2 + KOH + H_2O \rightarrow K_2HPO_4 + 2H_2$. Potassium phosphate is formed.

The simplest method of preparing the gas is by the action of water upon calcium phosphide:

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3.$$

This action is analogous to that of water upon magnesium nitride (p. 417) by which ammonia is produced. In consequence of the fact that calcium phosphide is a substance of irregular composition, a mixture of all three hydrides is generally obtained. By passing the gas through a strongly cooled delivery tube, however, the liquid compound is condensed and fairly pure phosphine passes on.

Phosphine is a colorless gas, which is easily decomposed by heat into its elements. When burned, it forms phosphoric acid. It is exceedingly poisonous and, unlike ammonia, it is insoluble in water, and produces no basic compound corresponding to ammonium hydroxide when brought in contact with this substance. It resembles ammonia, formally at least, in uniting with the hydrogen halides (see below). It differs from ammonia, however, inasmuch as it does not unite with the oxygen acids. Phosphine acts upon solutions of some salts, precipitating phosphides of the metals:

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4.$$

The **liquid hydrogen phosphide** boils at 57°. The molecular weight, as determined by the density of its vapor, shows the formula to be P_2H_4. It forms no salts, and is therefore quite unlike hydrazine. When exposed to light, it decomposes, giving phosphine and the solid hydride.

Phosphonium Compounds. — Hydrogen iodide unites with phosphine to form a colorless solid crystallizing in beautiful, highly refracting, square prisms: $PH_3 + HI \rightarrow PH_4I$. Hydrogen chloride combines similarly with phosphine, but only when the gases are cooled by a freezing mixture, or are brought together under a total pressure of 18 atmospheres at 14°. When the pressure is released, rapid dissociation occurs. This dissociation is one of the many cases where an action which absorbs heat, nevertheless goes on spontaneously (*cf.* p. 27). The indispensable fall in the energy of the system takes place by virtue of the diffusion of the constituents, and in amount this more than offsets the heat acquired.

In imitation of the ammonia nomenclature, these substances are called phosphonium iodide and phosphonium chloride. They are entirely different, however, from the corresponding ammonium derivatives, for the $PH_4^{\cdot}$ ion is unstable. When brought in contact with water they decompose into their constituents, the hydrogen halide going into solution, and the phosphine being liberated as a gas.

Halides of Phosphorus. — The existence of the following halides has been proved conclusively:

. . . .	. . . . .	. . . . .	P_2I_4 (solid)
PF_3 (gas)	PCl_3 (liquid)	PBr_3 (liquid)	PI_3 (solid)
PF_5 (gas)	PCl_5 (solid)	PBr_5 (solid)	. . . . .

These substances may all be formed by direct union of the elements. They are incomparably more stable than are the similar compounds of nitrogen. They are all decomposed by contact with water, and give an oxygen acid of phosphorus and the hydrogen halide (see below). This action was used in the preparation of hydrogen bromide (p. 231) and hydrogen iodide (p. 238).

Phosphorus trichloride is made by passing chlorine gas over melted phosphorus in a flask until the proper gain in weight has occurred. It is a liquid, boiling at 76°. When excess of chlorine is employed, **phosphorus pentachloride**, which is a white solid body, is

formed. When moist air is blown over any of these substances, the water is condensed to a fog by the hydrogen halide. In the case of the interaction of phosphorus pentachloride and water, phosphoric acid is formed:

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl.$$

With a limited supply of water the hydrolysis is not so complete, and phosphoryl chloride * (phosphorus oxychloride), a liquid boiling at 107°, is produced :

$$PCl_5 + HOH \rightarrow POCl_3 + 2HCl.$$

This interaction of phosphorus pentachloride and water is a perfectly general one, and takes place with most compounds containing hydroxyl. Thus, when alcohol (which differs from water in having ethyl (C_2H_5), instead of hydrogen, combined with hydroxyl) is poured upon it, ethyl chloride, phosphoryl chloride, and hydrogen chloride are formed :

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl.$$

The same action takes place with all carbon compounds containing hydroxyl, and is used as a means of showing the presence of this group in their structure. The reaction is shown by inorganic compounds also. Thus, anhydrous sulphuric acid gives sulphuryl chloride, which may be separated from the phosphoryl chloride by fractional distillation (see Petroleum) :

$$SO_2(OH)_2 + 2PCl_5 \rightarrow SO_2Cl_2 + 2POCl_3 + 2HCl.$$

Phosphorus pentachloride, when heated, reaches a vapor tension of 760 mm. at 140°, and while still solid. It therefore passes freely into vapor (boils, so to speak) at this temperature, and condenses directly to the *solid* form. This sort of distillation is called **sublimation**. At a pressure above that of the atmosphere it melts at 148°. This is simply a case in which the vapor tension of the solid, increasing with rise in temperature, happens to pass the arbitrary value of the opposing pressure (one atmosphere) peculiar to experiments carried on in open vessels, before the melting-point is reached. The same phenomenon is shown by sulphur trioxide (p. 381).

* This substance is a mixed anhydride (p. 397) of phosphoric acid and hydrogen chloride.

Phosphorus pentachloride (*cf.* p. 255) and pentabromide, when vaporized, are partially dissociated:

$$PBr_5 \rightleftarrows PBr_3 + Br_2.$$

Since the first two members of this equilibrium are colorless, while the bromine is brown, this action may be used to **illustrate** the effect upon a system, of **increasing the concentration of one of the interacting substances** (p. 249). Two tubes of equal volume and containing equal amounts of the pentabromide are prepared. A small amount of the tribromide is added to the second, and both are sealed up. When the tubes are now heated to the same temperature, the contents of the second will be less strongly colored by bromine in consequence of the greater activity in it of the reversing action.

Oxides of Phosphorus. — The oxides of phosphorus are the so-called trioxide P_4O_6, the pentoxide P_2O_5, and a tetroxide P_2O_4.

The **pentoxide** is a white powder formed when phosphorus is burned with a free supply of oxygen. It unites with water with great violence to form metaphosphoric acid (see below), and hence is known as **phosphoric anhydride**: $P_2O_5 + H_2O \rightarrow 2HPO_3$. In the laboratory this action is frequently utilized for drying gases (p. 101) and for removing water from combination (p. 276). The vapor density of the pentoxide indicates that its formula is P_4O_{10}, but its whole chemical behavior is equally well represented by the simpler formula.

The **trioxide** is obtained by burning phosphorus in a tube with a restricted supply of air. It is a white solid, melting at 22.5° and boiling at 173°. On account of the ease with which it may be volatilized, it can be separated by distillation from any pentoxide formed at the same time. The operation must be carried out in an apparatus from which the air is excluded, as the trioxide unites spontaneously with oxygen. The vapor density of the substance shows that its formula is P_4O_6. This formula is preferred to the simpler one because, although the oxide is the anhydride of phosphorous acid, it nevertheless unites exceedingly slowly with cold water to form this substance. It interacts vigorously with hot water, but phosphine, red phosphorus, hypophosphoric acid, and phosphoric acid are amongst the products, and very little phosphorous acid escapes decomposition. When this oxide is heated to 440° it decomposes, giving the compound P_2O_4 and red phosphorus.

Acids of Phosphorus. — There are four different acids of phosphorus in which, probably, four distinct stages of oxidation are shown. The highest stage is represented by three phosphoric acids, where the degree of hydration of the anhydride varies. These are orthophosphoric acid H_3PO_4, pyrophosphoric acid $H_4P_2O_7$, and metaphosphoric acid HPO_3. The other acids are less important. They are phosphorous acid (H_3PO_3), hypophosphoric acid ($H_4P_2O_6$), and hypophosphorous acid (H_3PO_2).

The Phosphoric Acids. — The relation between the three different phosphoric acids may be seen by considering them as being formed from phosphorus pentoxide and water. It will be remembered that in the majority of cases already considered, this sort of action takes place for the most part in but one way. Thus, nitric acid is known in but one form, which is produced by the union of one molecule each of nitrogen pentoxide and water : $N_2O_5 + H_2O \rightarrow 2HNO_3$. Similarly the chief sulphuric acid is the one formed from one molecule of sulphur trioxide and one molecule of water : $SO_3 + H_2O \rightarrow H_2SO_4$, although here we have both the hydrate H_2SO_4, H_2O, which might be written H_4SO_5 and disulphuric acid $H_2S_2O_7$. Referred to the anhydride these three acids are H_2O,SO_3, $2H_2O,SO_3$, and $H_2O,2SO_3$. Periodic acid (p. 278) has a set of even more complexly related acids or salts.

Now, when phosphoric anhydride acts upon water we obtain a solution which, on immediate evaporation, leaves a glassy solid, HPO_3, known as metaphosphoric acid. This is H_2O, P_2O_5. When, however, the solution is allowed to stand for some days, or is boiled with a little dilute nitric acid whose hydrion acts catalytically, the residue from evaporation is H_3PO_4, orthophosphoric acid :

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \quad \text{or} \quad HPO_3 + H_2O \rightarrow H_3PO_4.$$

This acid is $3H_2O$, P_2O_5, and no further addition of water can be effected.

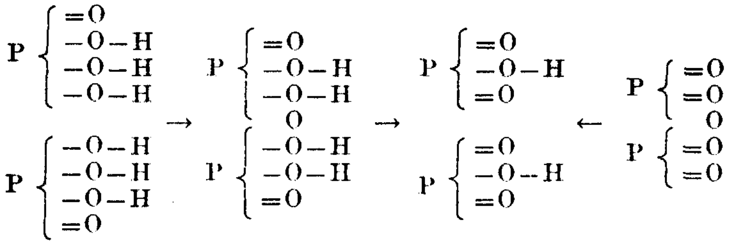
Conversely, when orthophosphoric acid is kept at about 255° for a time, it slowly loses water, and $H_4P_2O_7$, pyrophosphoric acid, is obtained :

$$2H_3PO_4 \rightarrow H_2O + H_4P_2O_7.$$

This acid is $2H_2O$, P_2O_5. Further desiccation leaves metaphosphoric acid, which cannot be further resolved into phosphorus pentoxide and water. When dissolved in water, pyrophosphoric acid slowly resumes

the water which it has lost and gives the ortho-acid again. The pyro-acid does not seem to be formed by hydration of the meta-acid, but only by dehydration of the ortho-acid.

The relations of all these substances are more clearly seen in the graphic formulæ:



The addition or removal of water leaves the valence of the phosphorus unchanged.

Pyrosulphuric acid and its salts when dissolved in water give sulphuric acid and acid sulphates respectively. That is to say, the ion S_2O_7 is not capable of existence. But the very slow rate at which the less hydrated phosphoric acids change into the more hydrated ones shows that ions like PO_4''', PO_3', and P_2O_7'''' may be comparatively stable. The behavior of solutions of the salts shows this even more clearly.

Orthophosphoric Acid and Its Salts. — As we have seen, ordinary calcium phosphate is the source of the impure, commercial acid. Pure orthophosphoric acid may be made by boiling red phosphorus with slightly diluted nitric acid and evaporating the water and excess of nitric acid. The product is a white, crystalline, deliquescent solid.

This acid is much weaker than sulphuric acid, and is dissociated chiefly into the ions $H^{\bullet}$ and H_2PO_4'. The dihydrophosphanion is broken up to some extent into $H^{\bullet}$ and HPO_4'', as we learn from the fact that the solution of the sodium salt NaH_2PO_4 is acid. The ion HPO_4'' is hardly dissociated at all, for a solution of the salt Na_2HPO_4 is alkaline in reaction.

As a tribasic acid, it forms salts of three kinds, such as NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. These are known respectively as **primary**, **secondary**, and **tertiary** sodium orthophosphate. The primary sodium phosphate is faintly acid in reaction. The secondary one is slightly alkaline, because of hydrolysis arising from the tendency of the

hydrion of the water to combine with the HPO_4'' to form H_2PO_4' (*cf.* p. 344). The tertiary phosphate is stable only in solid form, and can be made by evaporating to dryness a mixture of the secondary phosphate and sodium hydroxide:

$$Na_2HPO_4 + NaOH \rightleftarrows Na_3PO_4 + H_2O \uparrow .$$

When the product is dissolved in water, the action is reversed (*cf.* p. 375). Mixed phosphates are also known, particularly sodium-ammonium phosphate (microcosmic salt), $NaNH_4HPO_4$, and the insoluble magnesium-ammonium phosphate, $MgNH_4PO_4$.

Primary calcium phosphate, known in commerce as "superphosphate," is used as a fertilizer. On account of its insolubility, and since plants can take up soluble substances only, calcium phosphate is of relatively little service to plants. It is therefore converted into the "superphosphate," which is soluble, by treatment with dilute sulphuric acid:

$$Ca_3(PO_4)_2 + H_2SO_4 \rightleftarrows 2CaSO_4 + CaH_4(PO_4)_2 .$$

The tertiary phosphates are unchanged by heating. The primary and secondary phosphates, however, retaining, as they do, some of the original hydrogen of the phosphoric acid, are capable of losing water like phosphoric acid itself, when heated. The actions are slowly reversed when the products are dissolved in water:

$$NaH_2PO_4 \rightleftarrows NaPO_3 + H_2O,$$
$$2Na_2HPO_4 \rightleftarrows Na_4P_2O_7 + H_2O.$$

It will be seen that the meta- and pyrophosphates of sodium are formed by these actions; and this is indeed the simplest way of forming these substances, since the acids themselves are not permanent in solution, and are too feeble to lend themselves to exact neutralization. Ammonium salts of phosphoric acid lose ammonia, as well as water, when heated (*cf.* p. 421). Thus, microcosmic salt gives primary sodium phosphate:

$$NaNH_4HPO_4 \rightarrow NaH_2PO_4 + NH_3,$$

and this in turn is converted into the metaphosphate by loss of water.

Pyrophosphoric Acid. — This acid, obtained by heating orthophosphoric acid, may be prepared in pure form by making the sparingly soluble lead salt from sodium pyrophosphate, and precipitating

the plumbion by addition of sulphuric acid. In solution it gradually reunites with water. Although tetrabasic, having four hydrogen atoms which may be displaced by metals, only two kinds of salts of this acid are known. These are the normal salts, such as $Na_4P_2O_7$, and those in which one-half of the hydrogen has been displaced by a metal such as $Na_2H_2P_2O_7$.

Metaphosphoric Acid. — This is the "glacial phosphoric acid" of commerce, and is usually sold in the form of transparent sticks. It is obtained by heating orthophosphoric acid, or by direct union of phosphorus pentoxide with a small amount of cold water. It passes into vapor at a high temperature, and its vapor density corresponds to the formula $(HPO_3)_2$. The existence of certain complex salts confirms our belief in the existence of a tendency to association (p. 242).

Sodium metaphosphate $NaPO_3$, in the form of a small globule obtained by heating microcosmic salt on a platinum wire, is used in analysis. When minute traces of oxides of certain metals are placed upon such a globule, known as a **bead**, and heated in the Bunsen flame, the mass is colored in various tints according to the oxide used (**bead test**). This action may be understood when we consider that sodium metaphosphate takes up water to form primary sodium orthophosphate : $NaPO_3 + H_2O \rightarrow NaH_2PO_4$. In the same way, but at higher temperatures, it is able to take up oxides of elements other than hydrogen, giving mixed orthophosphates. Thus with oxide of copper a part of the metaphosphate unites according to the equation :

$$NaPO_3 + CuO \rightarrow NaCuPO_4,$$

and the product confers a green tinge on the bead.

Distinguishing Tests. — When a solution of nitrate of silver is added to a solution of orthophosphoric acid or any soluble orthophosphate, a yellow precipitate of silver orthophosphate Ag_3PO_4 is produced. This is a test for phosphanion. With pyrophosphoric acid or any pyrophosphate the product is white $Ag_4P_2O_7$. With metaphosphoric acid a white precipitate, $AgPO_3$, is obtained also. Metaphosphoric acid coagulates a clear solution of albumen, while pyrophosphoric acid has no visible effect upon it.

A test for orthophosphoric acid, or rather the ion PO_4''', consists in adding a drop of the solution containing this ion to a solution of ammonium molybdate (*q.v.*) in dilute nitric acid. A copious yellow precipitate of an ammonium phospho-

molybdate, $(NH_4)_3PO_4, 11MoO_3, 6H_2O$, appears on warming. In presence of excess of ammonia, the formation of the white insoluble ammonium-magnesium phosphate (p. 467) serves as a test also. Arsenic acid (*q.v.*) gives precipitates of appearance and composition similar to these two.

Phosphorous Acid. — With cold water phosphorus trioxide (P_4O_6) yields phosphorous acid very slowly. With hot water the action is exceedingly violent and complex (p. 464). This acid may be obtained also by the action of water upon phosphorus trichloride, tribromide, or tri-iodide and evaporation of the solution:

$$PCl_3 + 3H_2O \rightarrow P(OH)_3 + 3HCl.$$

A certain amount of this acid, along with phosphoric acid and hypophosphoric acid, is formed when moist phosphorus oxidizes in the air.

In spite of the presence of three hydrogen atoms, this acid is dibasic, and two only are replaceable by metals. To express this fact, the first of the following formulæ is preferred:

$$O = P\begin{cases} -H \\ -O-H \\ -O-H \end{cases} \qquad\qquad P\begin{cases} -O-H \\ -O-H \\ -O-H \end{cases}$$

since the symmetrical formula would indicate no difference between the three hydrogen atoms. H united directly to P, as here and in PH_3, is not acidic. Phosphorous acid is a powerful reducing agent, precipitating silver, for example, in the metallic form from solutions of its salts. When heated, it decomposes, giving the most stable acid of phosphorus (*cf.* pp. 268, 274, 395), namely, metaphosphoric acid, and phosphine:

$$4H_3PO_3 \rightarrow 3HPO_3 + 3H_2O + PH_3.$$

Hypophosphorous Acid. — The potassium salt of this acid is obtained, as we have seen, when phosphorus is heated with potassium hydroxide solution (p. 461). It may be prepared in the free form by substituting barium hydroxide for potassium hydroxide:

$$3Ba(OH)_2 + 8P + 6H_2O \rightarrow 3Ba(H_2PO_2)_2 + 2PH_3.$$

By careful addition of dilute sulphuric acid to the resulting liquid, barium sulphate is precipitated. On evaporation of the water the white crystalline acid, H_3PO_2, is obtained. This acid is monobasic; two of its hydrogen atoms cannot be displaced by metals. To ex-

press this fact the graphic formula $O = P\begin{cases} -H \\ -H \\ -OH \end{cases}$ is used. This substance is also a powerful reducing agent, tending, by the acquisition of oxygen, to pass into phosphoric acid.

Structural Formulæ of Salts of Hydrogen. — As a rule, the formulæ of acids have thus far been written with the ionizable hydrogen in front: HCl, H_2SO_4, $HC_2H_3O_2$. This is only one illustration of the method by which chemists have constantly sought to utilize formulæ for the purpose of expressing, not merely the composition of a substance, but some of its properties as well. By another typographical device we have attempted to indicate the behavior of dilute solutions by putting the radicals in brackets: $Cu(NO_3)_2$, $Ba(OH)_2$. These are called structural or constitutional formulæ, and their object is not to show actual structure, but to exhibit the modes of action of the substance, by means of a supposed structure. Now the modes of action of a single substance are often rather various, and one and the same structural formula cannot represent all of these at once. We have observed this, particularly, with the oxygen acids. Thus, $H_2.SO_4$ expresses the mode of activity in dilute solution and often when no solvent is present, as in the action on chlorides (p. 178) and nitrates (p. 439). But when all the hydrogen of an acid is not ionizable, we regard that which is so as part of an hydroxyl group in the parent molecules, and the rest as being attached to the characteristic non-metal of the acid, for example, the phosphorus (*cf.* pp. 391, 392). Thus, we should write phosphorous acid $POH(OH)_2$, instead of H_2PO_3H, to chronicle this fact. So also the formula $POH_2(OH)$ is used for hypophosphorous acid. Molecular actions, such as those of sulphuric acid $SO_2(OH)_2$ (p. 389), are well shown by these formulæ:

$$SO_2(OH)_2 + 2HBr \rightarrow SO_2 + 2H_2O + Br_2.$$

It must be noted particularly that this sort of formula, when the substance for which it stands is an acid, represents only some features in the behavior of the anhydrous substance and of the molecules, and not the ionic action in solution. A formula like $Ba(OH)_2$, where the material is a base, on the other hand, represents both the ionic and the molecular behavior. The graphic formula is more general (*cf.* p. 224). It shows all these relations, and often still others, but none of them so specifically.

Sulphides of Phosphorus. — Yellow phosphorus when heated with sulphur unites with explosive violence. By using red phosphorus the action can be controlled. By employing the proper proportions the **pentasulphide** P_2S_5 is secured. It is purified by distillation from a retort in which a current of carbon dioxide is maintained (see below). The distillate solidifies to a yellow crystalline mass, which melts at 274° and boils at 530°. Materials undergoing chemical change, which are to be kept at a constant, high temperature, are often placed in tubes suspended in the vapor of the pentasulphide. When a lower temperature is required, boiling sulphur (448°) is used.

Distillation in a stream of some inactive gas is a common means of distilling under reduced pressure (*cf.* p. 276). The dilution of the vapor lowers its partial pressure, just as would evacuation. This plan has the advantage, however, of sweeping the vapor away from the heated region into the condenser, and so diminishing the amount of decomposition. In dealing with compounds of carbon, a current of steam is often used for the above purposes. It enables us also to separate a slightly volatile substance from one which is almost involatile.

Phosphorus pentasulphide acts upon water in the cold, and upon substances containing hydroxyl when heated with them, the actions being similar to those of the pentachloride (p. 463):

$$P_2S_5 + 8H_2O \rightarrow 2H_3PO_4 + 5H_2S.$$

Other sulphides, P_4S_3, P_2S_3, and P_3S_6, may be prepared by using the constituents in the proportions represented by these formulæ.

Comparison of Phosphorus with Nitrogen and with Sulphur. — Although phosphorus and nitrogen are regarded as belonging to one family, the differences between them are more conspicuous than the resemblances. The latter are confined almost wholly to matters concerned with valence. The differences are seen in the facts that nitrogen is a gas and exists in but one form, while phosphorus is a solid occurring in two varieties, and that the former is inactive and the latter active. The contrasts between phosphine and ammonia (pp. 461–2) and between the halides of the two elements (p. 462) have been noted already. The pentoxide of nitrogen decomposes spontaneously; that of phosphorus is one of the most stable of compounds. Nitric acid is very active; the phosphoric acids are quite the reverse.

On the other hand, the resemblance of phosphorus to sulphur is

marked. Both are solids, existing in several forms. Both yield stable compounds with oxygen and chlorine. The hydrogen compounds interact with salts to give phosphides of metals and sulphides of metals, respectively. Against these must be set the facts, that hydrogen sulphide does not unite with the hydrogen halides at all, and that phosphoric acid is hard to reduce, while sulphuric acid is reduced with comparative ease.

Exercises. — 1. Explain the effect of sulphuric acid in setting fire to the earliest matches (p. 460).

2. Make a brief definition of a substance capable of sublimation (p. 463).

3. Why would a mixture of potassium dichromate and hydrochloric acid (p. 374) be less suitable than nitric acid for making phosphoric acid from red phosphorus?

4. Why is not the tertiary phosphate of sodium (p. 467) decomposed by heating? What tertiary phosphates would be decomposed by this means?

5. Formulate the hydrolyses of the secondary and tertiary sodium orthophosphates as was done for sodium sulphide (p. 375).

6. How should you prepare $Ca_2P_2O_7$ and $Ca(PO_3)_2$?

7. What product should you confidently expect to find after heating (*a*) sodium phosphite, Na_2HPO_3, (*b*) barium hypophosphite (p. 469)?

8. Compare the elements chlorine and phosphorus after the manner of the comparisons on p. 471.

CHAPTER XXVIII

CARBON AND THE OXIDES OF CARBON

The Chemical Relations of the Element. — The elements of the carbon family are carbon, silicon, germanium, tin, and lead. Of these the first two are entirely non-metallic, while the others are metals showing more or less strong resemblances to the non-metals. All these elements are quadrivalent as regards the maximum valence which they exhibit. With the exception of silicon, however, they all form compounds in which they are bivalent.

The chemistry of the compounds of carbon is an exceedingly extensive and complex subject. It is commonly known as organic chemistry, on account of the fact that the majority of the substances composing, and produced by, living organisms are compounds of carbon, and that it was at first supposed that their artificial production, *e.g.* without the intervention of life, was impossible. But many natural organic products have now been made from simpler ones or from the elements, a process called **synthesis**, and the preparation of the others is delayed only in consequence of difficulties caused by their instability and complexity. On the other hand, hundreds of compounds unknown to animal or vegetable life, including many valuable drugs and dyes, have now been added to the catalogue of chemical compounds.

The elements entering into carbon compounds are chiefly hydrogen and oxygen. After these, nitrogen, the halogens, and sulphur may be named.

CARBON.

Occurrence. — Large quantities of carbon are found in the free condition in nature. The diamond is the purest natural carbon, and at the same time the least plentiful. Graphite, or plumbago, which is the next purest, is found in limited amounts, and is a valuable mineral. Coal occurs in numerous forms containing greatly varying proportions of free carbon. Small quantities of the free element have been found in meteorites.

In combination, carbon is found in marsh-gas, or methane CH_4, which is the chief component of natural gas. The mineral oils consist

almost entirely of mixtures of various compounds of carbon and hydrogen. Whole geological formations are composed of carbonates of common metals, particularly calcium carbonate or limestone, and a double carbonate of calcium and magnesium, known as dolomite.

The Diamond. — The varieties of carbon differ very markedly in their physical properties, and to some extent also in their chemical behavior. Diamonds, which are found in India, Borneo, Brazil, and South Africa, are scattered sparsely through metamorphic and volcanic rocks which seem to have undergone secondary changes. They are covered with a crust which entirely obscures their luster, and possess natural crystalline forms belonging to the regular system. A form related to the octahedron is frequently observed. It should be noted that this natural form bears no relation whatever to the pseudo-crystalline shape which is conferred upon the stone by the diamond-cutter. Thus, a "brilliant" possesses one rather large, flat face, which forms the base of a many sided pyramid (Fig. 91, showing two views). This form is given to the stone, in order that the maximum reflection of light from its interior may be produced. The diamond is harder than any other variety of matter, with the exception, perhaps, of one compound of boron, while only one or two other materials, like carborundum, approach it. It may be remarked in passing, that the hardness of a substance is measured, on an arbitrary scale, by the way in which it is able to scratch smooth surfaces of other bodies. The corner of one of the natural diamond crystals will scratch the surface of almost every other substance, while its surfaces in turn are scratched by carbide of boron alone. Its specific gravity is about 3.5, and it is the densest form of carbon. Few materials are capable of dissolving any of the forms of carbon. Molten iron (*q.v.*) dissolves five or six per cent, part of which goes into combination, and a few other substances at high temperatures dissolve much smaller quantities. The diamond is a nonconductor of electricity.

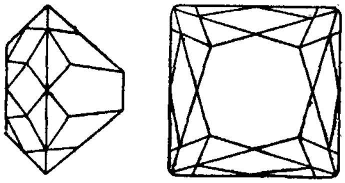


Fig. 91.

The largest diamond known, the *Jubilee*, was exhibited at the Paris Exposition of 1900, and weighed 49 g. The *Kohinoor* weighs 22 g. The diamond, although its origin in nature is still a matter of uncertainty, has been made artificially in several ways. Moissan (1887)

dissolved carbon in molten iron and, after chilling the mass so as to produce a solid crust, which by its shrinkage severely compressed the interior, allowed the whole to cool very slowly. Portions of the interior of the ingot were treated with acid to dissolve the iron, and amongst the insoluble particles were recognized a few microscopic fragments (none larger than 0.5 mm.) which exhibited the form and hardness of the diamond. The greater part of the carbon, however, appeared as graphite.

That the diamond contains nothing but carbon, is shown by the fact that when burned it produces nothing but carbon dioxide.

Graphite. — Graphite (Gk. γράφω, I write) is found in Cumberland, Siberia, Ceylon, and elsewhere. Good crystals are seldom found, but the form appears to belong to the hexagonal system. The mineral is extremely soft, in utter contrast to the diamond, and has a smaller specific gravity (about 2.3). It conducts electricity. It is now made artificially by an electro-thermal process (*cf.* p. 457). A powerful alternating current is passed through a mass of granular anthracite, and the latter, although not melted by the high temperature, is largely converted into graphite.

Graphite is now used exclusively for making the anodes in the electrolytic manufacture of chlorine and in related processes. Mixed with fine clay it forms the "lead" of lead pencils. As "black-lead", it is employed to protect ironware from rusting. It takes the place of oil as a lubricant in cases where the former would be decomposed by heat. The fine, slippery scales, which it forms when pulverized, fill the inequalities in the bearings, and glide over one another with little friction.

Amorphous Carbon. — This is the name given to the varieties of the element which have no crystalline form. They vary in specific gravity up to 1.9. **Coke**, which is now manufactured in immense quantities by heating coal until all the volatile matter has been distilled off, is a very dense variety of amorphous carbon. It is used in the reduction of iron ores. The value of coking lies largely in the removal of the sulphur, originally contained in the coal in the form of pyrite.

By the imperfect combustion of heavy oils and resins, in which the flame plays upon a cooled surface, a finely divided form of carbon

known as **lampblack** is produced. This is much used in the manufacture of printer's ink.

Charcoal is chiefly made by the heating of wood out of contact with air. In the more refined forms of the process the charring is conducted in retorts, and the materials which distil off are used in various ways. Wood consists largely of cellulose $(C_6H_{10}O_5)_n$, incrusted with lignin and holding much moisture and resinous material. The products of its distillation are partly gaseous and partly fluid. The gases, consisting mainly of hydrogen, methane CH_4, ethane C_2H_6, ethylene C_2H_4, and carbon monoxide CO, are employed, on account of their combustibility, as fuel in the distillation itself. The fluids form a complex mixture containing large quantities of water, wood spirit, or methyl alcohol CH_3OH, acetic acid, acetone $(CH_3)_2CO$, and tar. Wood charcoal exhibits the cellular structure of the material from which it was made, and is therefore exceedingly porous. The original mineral constituents of the wood appear in the ash of the charcoal when the latter is burned.

For certain purposes, charcoals made in the same fashion as the above from bones and from blood, find wide application. The former, called **bone black** (p. 456), contains much calcium phosphate. In the chemical laboratory, **pure carbon** is made, as a rule, by the charring of sugar (cane-sugar, $C_{12}H_{22}O_{11}$). The sugar is purified from mineral matter, before use, by crystallization from water.

The tendency of almost all carbon compounds to char, when heated, is used as a means of recognizing their presence.

Properties of Charcoal. — Charcoal exhibits certain properties which are not shared to any extent by other forms of carbon. For example, it can take up large quantities of many gases. Boxwood charcoal will in this way absorb ninety times its own volume of ammonia, fifty-five volumes of hydrogen sulphide, or nine volumes of oxygen. Freshly made dogwood charcoal (used in making the best gunpowder), when pulverized immediately after its preparation, often catches fire spontaneously on account of the heat liberated by the condensation of oxygen. It is therefore set aside for two weeks, to permit the slow absorption of moisture and air, before being ground up. The absorbed gases may be removed unchanged by heating the charcoal in a vacuum. The disappearance of these immense quantities of gas into small pieces of charcoal is described as **adsorption**, and is caused by the *ad*hesion of the gases to the very extensive internal surface

which the charcoal possesses. Solid and liquid bodies are also in many cases taken up by charcoal in a similar fashion. Thus, strychnine may be removed from an aqueous solution by agitation of the latter with charcoal. In the manufacture of whiskey (*q.v.*), the fusel oil, which is extremely harmful, is in many cases removed by filtration of the diluted spirit through charcoal, before rectification. Organic coloring matters, such as litmus and indigo, belong to the class of bodies thus extracted from solution by charcoal. In the refining of sugar the syrup is boiled with charcoal for the purpose of removing a brown resin, in order that the product may be perfectly white. It is, in part, upon this property that we rely, also, in the employment of charcoal filters. The organic materials dissolved in the drinking water undergo adsorption in the charcoal. In this connection, however, it must be remembered that the quantity which a given mass of charcoal may take up is limited, and that careful cleansing is required in order that the efficiency of the filter may be maintained.

Coal. — Peat, brown coal, soft coal, and anthracite represent, in a general way, different stages in the decomposition of vegetable matter in absence of air. Water and compounds of carbon and hydrogen are given off in the process. The ratio which the carbon combined with oxygen and hydrogen bears to the free carbon decreases in the order in which the substances stand above. The following table shows this change in composition and the relations of the substances to fresh wood on the one hand and charcoal and coke on the other:

	Percentage, excluding Ash and Moisture, of:				Percentage Ash.	Percentage of Water (Air Dried).	Calorific Value per g. in Calories.
	C	H	O	N			
Wood	45	6	48	1	1.5	18–20	2700
Peat	60	6	32	2	5—20	20–30	3500
Brown coal	70	5	24	1	3—30	15	30–6000
Soft coal	82	5	12	1	1—15	4	66–8000
Anthracite	94	3	3	..	1.5	2	70–8000
Charcoal	95	1.7	3.4	..	4	6.5	8080
Coke	96	0.7	2.5	1	3.4—11	2	7700

Chemical Properties of Carbon. — Diamond, graphite, and amorphous carbon probably differ from one another, not merely in physical properties, but also chemically. Certainly the stability of

tion in the tissues of plants and animals, leads to the formation of the same product.

It was Joseph Black (1757) who first recognized the gas as a distinct substance. He observed its formation when marble or magnesium carbonate was heated:

$$CaCO_3 \rightleftarrows CaO + CO_2,$$

and named the gas "fixed air" from the fact that it was contained in these solids. The above action had been used for centuries in making quicklime (calcium oxide). All common carbonates, excepting the normal carbonates of potassium and sodium, decompose in this way, leaving the oxide of the metal.

Black found that the gas was also produced when acids acted upon carbonates, and this method is commonly employed in the laboratory:

$$\left.\begin{array}{r} CaCO_3\text{ (solid)} \leftrightarrows CaCO_3\text{ (diss'd)} \leftrightarrows Ca^{\cdot\cdot} + CO_3'' \\ 2HCl\text{ (diss'd)} \leftrightarrows 2Cl' + 2H^{\cdot} \end{array}\right\} \leftrightarrows H_2CO_3 \leftrightarrows H_2O + CO_2.$$

Since the carbonic acid is very slightly ionized, the action is like that of acids on sulphites (p. 398). The carbonate of calcium, however, is very slightly soluble, so that an additional equilibrium controls its solution. In this respect the action is like that of acids on ferrous sulphide (p. 371).

Carbon dioxide is also a product of the fermentation of sugar (*q.v.*), as Black had the credit of showing.

Physical Properties. — Carbon dioxide is a colorless, odorless gas. It is much heavier than air. The G.M.V. weighs 44 g. The critical temperature is 31.1°. Liquefied carbon dioxide boils at −79°. The sp. gr. of the liquid at 0° is 0.95. At 0° its vapor tension is 35.4 atmospheres and at 20° 59 atmospheres. It must be preserved, therefore, in very strong, wrought-iron cylinders. Large quantities of it, often collected from fermentation vats, are sold in such cylinders, and used in operating beer-pumps and in making aerated waters. When the liquid is allowed to flow out into an open vessel it cools itself by its own evaporation and forms a white, snowlike mass. Solid carbon dioxide evaporates without melting (*cf.* p. 463). A mixture of solid carbon dioxide with ether is frequently used as a freezing mixture (−80°). The ether is employed to secure better contact with the body to be cooled.

The great contrast in the speeds of a chemical change at two temperatures (*cf.* p. 72) may be illustrated by putting a minute piece of sodium in some 30 per cent hydrochloric acid which has been cooled in the above mixture. Hardly any interaction can be observed. But if the temperature of the acid is allowed to rise, the action becomes more and more rapid, and ends by being explosively violent.

Carbon dioxide gas under a pressure of 760 mm. and at a temperature of 15° dissolves in its own volume of water. Up to pressures of four or five atmospheres Henry's law describes its solubility accurately. An aqueous solution, prepared under a pressure of 2–3 atmospheres, is familiarly known as *soda water*.

Chemical Properties. — Carbon dioxide is a stable compound, and shows a little dissociation only at the highest temperatures: $2CO_2 \rightleftarrows 2CO + O_2$.

The most active metals, such as potassium, sodium, and magnesium, burn brilliantly when heated in carbon dioxide, producing the oxide of the metal and free carbon. Less active metals, such as zinc and iron, give an oxide of the metal and carbon monoxide (*q.v.*).

Carbon dioxide unites directly with many oxides, particularly those of the more active metals, such as the oxides of potassium, sodium, calcium, etc. Hence the decomposition of calcium carbonate by heating (p. 480) is a reversible action, which proceeds in the opposite direction when a sufficient pressure of carbon dioxide is employed (*cf.* p. 256 and Chap. xxxv).

Carbon dioxide, when dissolved in water, forms an unstable acid:

$$H_2O + CO_2 \rightleftarrows H_2CO_3.$$

The name carbonic acid is frequently, though improperly, given to the gas itself, which is really the anhydride of the acid and has no acid properties.

Chemical Properties of Carbonic Acid. — The solution of carbon dioxide in water exhibits the properties of a weak acid. It conducts electricity, although not well. It turns litmus red, though not so decidedly as do strong acids. Its feebleness is due, however, not exclusively to the small degree of ionization, but also to the fact that ordinary solutions of carbon dioxide are necessarily very dilute. The ionization takes place chiefly according to the equation:

$$H_2CO_3 \rightleftarrows H^{\cdot} + HCO_3'.$$

In a deci-normal solution, less than two molecules of the acid in a thousand are ionized. The conditions of equilibrium between the gas and the solution are precisely similar to those described under sulphurous acid (p. 393).

Carbonates. — When excess of an aqueous solution of carbonic acid is mixed with a solution of a base like sodium hydroxide, or, as the operation is more usually performed, when carbon dioxide is passed directly into a solution of the alkali, water is formed and the carbonate remains dissolved:

$$H_2CO_3 + NaOH \leftrightarrows H_2O + NaHCO_3, \text{ or } H^{\cdot} + OH' \rightarrow H_2O.$$

The product is sodium hydrogen carbonate (sodium bicarbonate). Although technically an acid salt, its solution is neutral on account of the exceedingly slight dissociation of the HCO_3' ion. By addition of an equivalent of sodium hydroxide to the solution of the bicarbonate the normal carbonate is obtained :

$$NaOH + NaHCO_3 \rightleftarrows H_2O + Na_2CO_3.$$

This solution is alkaline in reaction, for the same reason that a solution of secondary sodium orthophosphate is so (*cf.* p. 466).

The carbonates, with the exception of those of potassium, sodium, and ammonium, are insoluble in water, and may be obtained by precipitation when the proper ions are employed. For example :

$$MgSO_4 + Na_2CO_3 \rightleftarrows MgCO_3 \downarrow + Na_2SO_4 \text{ or } Mg^{\cdot\cdot} + CO_3'' \rightleftarrows MgCO_3 \downarrow.$$

The aqueous solution of carbon dioxide interacts with solutions of barium and calcium hydroxides in a similar manner :

$$Ca(OH)_2 + H_2CO_3 \leftrightarrows CaCO_3 \downarrow + H_2O.$$

The formation of precipitates with these solutions is used as a test for carbon dioxide and a means of estimating its amount in a sample of air (*q.v.*).

Excess of carbon dioxide converts calcium carbonate into the more soluble bicarbonate, and hence considerable quantities of "lime" are frequently held in solution by natural waters:

$$H_2CO_3 + CaCO_3 \rightleftarrows H_2Ca(CO_3)_2.$$

A considerable excess of carbon dioxide is required to convert the whole of the carbonate into the soluble bicarbonate, since the action

is markedly reversible. In the same fashion, the carbonates of iron ($FeCO_3$), magnesium, and zinc are somewhat soluble in water containing free carbonic acid. In fact, the solution, transportation, and deposition of all these carbonates take place in nature on a large scale by the alternate progress and reversal of this action. Water containing calcium carbonate in solution is known as *hard water* (*q.v.*), that containing ferrous carbonate as *chalybeate*, or *iron water*.

Rôle of Chlorophyl-bearing Plants in Storing Energy. — While in plants the same consumption of oxygen and production of carbon dioxide goes on as in animals, only with less rapidity, an action which is in a general way a reversal of this takes place at the same time. The chlorophyl and protoplasm in the leaves of the plant have the power of taking up carbon dioxide. Part of the oxygen is restored to the air, and the rest of the substance, including all the carbon, is used by the plant as food. This operation goes on only in sunlight (see below). The details of the chemical changes are not thoroughly understood, but the various chemical compounds which plants construct in large quantities, of which, sugar, starch, and cellulose are prominent examples, are built up as the result of this action. In a rough fashion, and disregarding the steps by which the process takes place, we may represent the chemical change by means of the thermochemical equation:

$$6CO_2 + 5H_2O \rightarrow C_6H_{10}O_5 + 6O_2 - 671{,}000 \text{ calories.}$$

Since the production of carbon dioxide by the combustion of any organic compound gives out heat, the partial reversal of this combustion, of which the green parts of the plant are the scene, requires the expenditure of energy, and the source of this energy is to be found in the sunlight. The difference in total energy between water and carbon dioxide, on the one hand, and the cellulose, starch, or sugar and free oxygen on the other, is very considerable. The above figures indicate roughly (p. 79) this difference (= the amount of energy stored) for cellulose, and the values for the other compounds are of the same order.

The importance of this remarkable endothermal action, involving the storing of the energy of sunlight, is very great. Aside from a little work done by water-power, the whole energy used by man and by animals comes from the reversal of it. The compounds forming the structure of the plant are employed in several different ways for

this purpose. When consumed by herbivora as food, the chemical changes which they undergo furnish the energy necessary for the continued life of the organism. The whole of the material is not at once reduced to the state of carbon dioxide, but passes into other forms of combination, which in turn become the food of the carnivora, or flesh-eating animals. By the oxidation to carbon dioxide which takes place in the bodies of these animals, the process of exhausting the possible energy of the carbon compounds is completed.

In another fashion we secure energy from the materials of plants by burning wood and employing the heat thus produced. In still another fashion, after the wood has undergone partial decay and conversion into coal, we secure the remaining energy which this contains by its final combustion in the furnace of the steam-engine.

It should be noted that the energy in the last case is not stored exclusively in the coal, but is shared between carbon and the oxygen of the air. If our atmosphere consisted of compounds of carbon, then the material corresponding to stores of coal would have to be oxygen or compounds of oxygen, and we should be likely then to speak of the energy as being stored for us and sold in the form of oxygen. That we are in the habit of speaking of it, at present, as going with the carbon is because the oxygen of the air is supplied free of charge, while the coal and wood have to be purchased.

Photochemical Action. — We have seen that light may simply act catalytically, as on a mixture of hydrogen and chlorine (p. 174) or an aqueous solution of hypochlorous acid (p. 268). These actions involve the liberation of energy and go on spontaneously (*cf.* p. 271) under proper conditions. On the other hand, light may actually be consumed in large amount in producing a chemical change, as in decomposing silver chloride (p. 14), or in the above instance. All wave lengths of light, which is the same as to say all colors of light, are not equally active in any one case. But there is no particular set of wave lengths which is of special chemical activity. In the action on silver chloride, green and blue light is very active, while red is almost without effect. Here, in the actions in which chlorophyl is concerned, it is the red and yellow light that produces the chemical change, and a plant exposed to blue light (*e.g.*, by shading with blue glass) will assimilate none of the carbon dioxide in the air surrounding it. The chemical substances in the retina of the eye seem to resemble those in the leaves of plants, for they are most affected by red and yellow light. To put this another way, a spectrum of uniform intensity throughout, when

viewed by a plant or a human eye, would appear to be brightest in the red and yellow portions, while a considerable stretch towards the blue extremity would actually be invisible. On the other hand, to an eye in which the active substance was silver chloride, if such an eye could be imagined as existing, the red end would be invisible and the blue and ultra-violet would be the most brilliant parts.

Carbon Monoxide.

Preparation. — Carbon monoxide is formed in many industrial operations. We commonly observe the blue flame of burning carbon monoxide playing on the surface of a coal fire. The gas is produced by the passage of the carbon dioxide, which is first formed, through the upper layers of heated coal:

$$CO_2 + C \rightarrow 2CO.$$

A similar reduction of carbon dioxide is produced by metals such as zinc, when a moderate heat is applied:

$$CO_2 + Zn \rightarrow ZnO + CO.$$

On a large scale, a mixture of carbon monoxide and hydrogen is prepared as the basis of **water gas**. Steam is turned into an iron cylinder lined with fire clay and filled with vigorously burning coke:

$$C + H_2O \rightarrow CO + H_2.$$

The products are both combustible, and, by the addition of substances which burn with a luminous flame, the mixture is used for the manufacture of illuminating-gas (*q.v.*).

In the laboratory, carbon monoxide is frequently obtained by heating oxalic acid, a solid, white, crystalline substance, with concentrated sulphuric acid. The latter is here employed simply as a dehydrating agent (p. 388), so that it need not be included in the equation:

$$H_2C_2O_4 \rightarrow CO_2 + CO + H_2O.$$

To obtain pure carbon monoxide from this mixture it is necessary to remove the carbon dioxide and to dry the gas. The carbon dioxide may be absorbed by passing the gas through a concentrated solution of potassium hydroxide. By treatment of formic acid, or sodium formate, with sulphuric acid, the presence of the carbon dioxide may be avoided:

$$HCHO_2 \rightarrow CO + H_2O.$$

Physical Properties. — Carbon monoxide is a colorless, tasteless, odorless gas. It is very slightly soluble in water. Its density is almost the same as that of air, for the G.M.V. weighs 28 g. When liquefied it boils at $-190°$.

Chemical Properties. — All the chemical properties of carbon monoxide are referable to the fact that in it the element of carbon appears to be bivalent: $C=O$. The compound is in fact unsaturated, and combines with oxygen, chlorine, and other substances directly. Thus the gas burns in the air, uniting with oxygen to form carbon dioxide. Again, iron (*q.v.*) is manufactured by the reduction of the oxide of iron by gaseous carbon monoxide in the blast furnace:

$$Fe_2O_3 + 3CO \rightleftarrows 2Fe + 3CO_2.$$

In sunlight carbon monoxide unites directly with chlorine to form carbonyl chloride $COCl_2$. It is absorbed by a solution of cuprous chloride in hydrochloric acid or ammonium hydroxide, forming a compound whose composition is probably represented by the formula $Cu_2Cl_2,CO,2H_2O$. It unites directly with certain metals, notably nickel and iron, with which it forms the so-called nickel carbonyl and iron carbonyl, respectively. The former is a colorless, volatile liquid $Ni(CO)_4$.

The gas is an active poison. When inhaled it unites with the hæmoglobin of the blood to the exclusion of the oxygen or carbon dioxide, each of which forms less stable compounds (*cf.* p. 432). A quantity equivalent to about 10 c.c. of the gas per kilo. weight of the animal is sufficient to produce death, about one-third of the whole hæmoglobin having entered permanently into combination with carbon monoxide.

The quantities of heat given out by the successive unions of two units of oxygen with one unit of carbon are worth recording:

$$C + O \longrightarrow CO + 2630 \text{ calories},$$
$$CO + O \longrightarrow CO_2 + 6830 \text{ calories}.$$

It will be seen that the addition of the second atom of oxygen appears to cause the evolution of a very much larger amount of heat than does that of the first. It must be remembered, however, that the carbon monoxide is gaseous, while the carbon in the first equation is solid, and probably in a condition of complex molecular aggregation. The heats produced by the unions of the two units are probably not very different, but in the first case a large amount of the heat is used up in disintegrating the carbon and bringing it into the gaseous condition.

CARBONYL CHLORIDE AND UREA.

Carbonyl Chloride. — This substance is also named **phosgene** (Gk. φῶς, light; γεννᾶν, to produce), on account of its formation by the catalytic influence of sunlight (p. 484). On a commercial scale it is obtained by passing the mixed carbon monoxide and chlorine over animal charcoal, which assists the union catalytically. It is a liquid which boils at 8°, possesses a suffocating odor, and is very soluble in benzene and some other hydrocarbons. When brought into contact with water it is hydrolyzed at once, forming carbonic acid and hydrochloric acid:

$$COCl_2 + 2H_2O \rightarrow H_2CO_3 + 2HCl.$$

Urea. — When ammonia and carbonyl chloride are mixed in the proper proportions, urea, a most interesting chemical substance, is produced:

$$O{=}C\begin{matrix}\diagup Cl \\ \diagdown Cl\end{matrix} + \begin{matrix}H-NH_2 \\ H-NH_2\end{matrix} \rightarrow O{=}C\begin{matrix}\diagup NH_2 \\ \diagdown NH_2\end{matrix} + 2HCl$$

Excess of ammonia has to be used to combine with the hydrogen chloride thus set free, so that the final equation is:

$$COCl_2 + 4NH_3 \rightarrow CO(NH_2)_2 + 2NH_4Cl.$$

The urea, a white, crystalline solid, is soluble in alcohol, while ammonium chloride is not, so that the former may be washed out by means of this solvent and recovered by evaporation. A little reflection will show that, using the above action as the final stage, urea can be built up from the simple substances composing it.

Urea was known long before any method for its synthesis had been discovered. It is the chief product of the decomposition of compounds of nitrogen in the animal body, and is found in the liquid excrements of animals. It was regarded as a typical organic substance, in the old sense of the word (p. 473). In 1828 Wöhler succeeded in preparing it artificially (see below). This was the first synthesis by a chemist, of a true "organic" substance, and its preparation proved to be the precursor of many discoveries of a similar nature. From a later year, about 1840, we may date the transition of organic chemistry, a science in which the mystery of life was supposed to be supreme, into the chemistry of the compounds of carbon, which is a branch of inorganic chemistry.

Wöhler used ammonium cyanate (*q.v.*), a substance in whose preparation we are independent of all products of life processes. When ammonium cyanate, or a mixture of any ammonium salt with potassium cyanate in solution in water, is warmed for some time, an intramolecular change (*cf.* p. 15) takes place, and long prisms of urea are deposited as the liquid cools:

$$NH_4.CNO \rightleftarrows CO(NH_2)_2.$$

Since the action is reversible, about four or five per cent of the ammonium cyanate remains unchanged.

The two substances just mentioned are entirely different in chemical properties. Ammonium cyanate is a highly ionized salt, while urea is not a salt at all, but a substance like ammonia which unites with acids to form salts. Materials which, like these, have the same composition and the same numbers of units in their molecules, and yet possess different properties, are spoken of in chemistry as **isomers**. The formulæ we have employed attempt to explain the differences in their properties by suggesting a difference in their molecular structure (*cf.* p. 224).

Assisted by the catalytic action of certain ferments, urea, when dissolved in water, can take up two molecules of the solvent to form ammonium carbonate:

$$CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftarrows 2NH_3 + H_2O + CO_2.$$

Ammonium carbonate (*q.v.*) is a somewhat unstable compound, and in turn, gives off ammonia and carbon dioxide. To this action is due in part the pronounced odor of ammonia arising from the decomposition of sewage.

Carbon Disulphide. — This compound is used in inorganic chemistry chiefly as a solvent. It is made by direct union of sulphur vapor and glowing charcoal. An electro-thermal method of carrying this out employs a furnace like that in Fig. 90 (p. 457). The substance comes off as a vapor and is condensed.

Carbon disulphide is a colorless, highly refracting liquid. When pure it possesses a pleasant odor, but traces of other compounds give the commercial article a disagreeable smell. It boils at 46° and burns in air, forming carbon dioxide and sulphur dioxide. Iodine, phosphorus, sulphur, rubber, and other substances dissolve freely in it.

Exercises. — 1. To which of the factors in the interaction of calcium carbonate and hydrochloric acid (p. 480) is due the forward displacement of all the equilibria?

2. What will be the excess of pressure inside a bottle of soda-

water when four volumes of carbon dioxide are dissolved in one volume of water?

3. What volume of liquid carbon dioxide, measured at 0°, will be required to give 75 liters of the gas at 0° and 760 mm. pressure?

4. What will be the effect of increase in pressure on the dissociation of carbon dioxide (p. 481)?

5. Prepare a diagram showing the whole scheme of equilibria involved in the hydrolysis of sodium carbonate (p. 482).

CHAPTER XXIX

SOME CARBON COMPOUNDS

THE compounds of carbon with hydrogen are called **hydrocarbons**. Those containing oxygen as well are divided into numerous and extensive groups according to their behavior. Thus there are **acids** like acetic acid, **carbohydrates** like sugar and starch, **alcohols** like common (ethyl) alcohol, **esters** like ethyl acetate and fat, **ethers** like common (ethyl) ether, and **bodies related to cyanogen** like prussic acid. We can discuss only one or two examples from each of the groups named.

THE HYDROCARBONS.

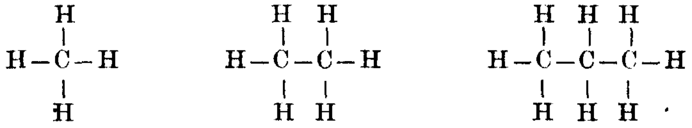
More than two hundred and fifty compounds of carbon and hydrogen have been described. They fall into several distinct series, the chief one of which contains methane CH_4 as its simplest member. On account of the fact that certain members of this set are found in paraffin, it is commonly known as the **paraffin series**. For the reason that in this series the carbon has all its four valences employed, the members are also called the **saturated hydrocarbons**.

Paraffin Series of Hydrocarbons. — The following list gives the formulæ of a few members of this series, with their names and their boiling-points or melting-points:

CH_4	methane	b.-p.	− 164°	Gases
C_2H_6	ethane	"	− 89.5°	
C_3H_8	propane	"	− 37°	
C_4H_{10}	butane	"	1°	
C_5H_{12}	pentane	"	35°	Liquids
C_6H_{14}	hexane	"	71°	
C_7H_{16}	heptane	"	99°	
.			.	
.			.	
.			.	

$C_{16}H_{34}$ . . .	hexadecane	m.-p.	18°	b.-p. 287.5°
.			.	
.			.	
$C_{35}H_{72}$ . .	pentatriacontane . . .	"	74.7°	Solids
.			.	
.			.	
$C_{60}H_{122}$ . .	hexacontane (dimyricyl) .	"	102°	

It will be noted that the hydrocarbons up to butane are gases. From pentane to hexadecane they are liquids. The remainder are solids. In composition each is related to the preceding one by containing the additional units CH_2. The formula of any member of the series is therefore representable by the expression C_nH_{2n+2}. Substances related in this way form an **homologous series**. Their relations will be more clearly perceived if we employ the graphic formulæ. Since hydrogen appears uniformly to be univalent, the carbon must form the backbone of each of the compounds. The formulæ of the first members are therefore as follows:



Transferences of H one step to the right and interpositions of CH_2 constitute the successive differences.

A large number of these substances occur in nature. Methane is present in large, and ethane in small, proportion in the natural gas of Pennsylvania and Ohio. Many of the others occur in petroleum.

Petroleum. — This oil consists of a mixture of the liquid and solid members of the series in varying proportions, and is found in many parts of the United States, in Ontario, at Baku on the Caspian, in India, and in Japan. In oil-refining, advantage is taken of the differences in the boiling-points to make a partial separation of the components by fractional distillation (see below). The compounds containing sulphur which are often present, and would give the obnoxious sulphur dioxide when the oil was burned, are deprived of this constituent by heating the oil with powdered cupric oxide. The unsaturated hydrocarbons (*q.v.*) are removed by agitation with concentrated sulphuric acid. The following are some of the products of the oil refinery, with their components and uses.

Name.	Components.	B.-P.	Uses
Petroleum ether	Pentane-hexane	40°– 70°	Solvent, gas-making
Gasolene	Hexane-heptane	70°– 90°	" "
Naphtha	Heptane-octane	80°–120°	" fuel
Benzine	Octane-nonane	120°–150°	"
Kerosene	Decane-hexadecane	150°–300°	Illuminating-oil

The portions of still higher boiling-point are employed as lubricating oils.

The vapor of these products is more inflammable the more volatile the components. The sale of kerosene is controlled legally by the requirement that the vapor it gives when heated shall not catch fire from a naked flame until the oil has reached a certain minimum temperature, the "flash point." This varies from 37.7° to 68.5° in different states and countries.

By cooling the residues from the retorts with a freezing mixture (*cf.* p. 164), some of the solid members of the series, $C_{22}H_{46}$ to $C_{28}H_{58}$, are obtained as white flakes, which are separated by filtration in presses. This material forms the paraffin used in waterproofing paper, in laundry work, and as an ingredient in candles. In some cases vaseline, consisting of substances melting at 40°–50°, $C_{22}H_{46}$ to $C_{28}H_{48}$, is obtained also.

From **ozocerite**, which is a sort of natural paraffin, ceresin, a substitute for beeswax, is made. **Asphalt** is another natural mixture of hydrocarbons.

The formation of these hydrocarbons in nature is not yet thoroughly explained. According to one theory, they are formed by the action of water upon carbides of metals; while according to another, they result from the decomposition of vegetable or animal matter. Possibly both of these sources have contributed to their formation. Certain differences between the natural oils of different localities point, at all events, to some difference in their origin.

Fractional Distillation. — When the boiling-points of two components of a liquid are very far apart, the vapor pressure of the one may be very low when that of the other, by heating, has reached 760 mm. In this case the first distillate will contain little of the high-boiling component. When, as in the case of petroleum, the differences in boiling-points are not great, complete separation of the

components is impossible. Yet by distillation in which the distillate is caught, not in one vessel, but in several successively, "fractions" are obtained such that the earlier ones contain more of the low-boiling and the later ones more of the high-boiling materials. The vessels are changed when the thermometer immersed in the vapor (Fig. 16, p. 38) reaches certain temperatures. When these fractions are then distilled one at a time, beginning with the lowest, and the several distillates are divided from one another by the same temperatures as before, a more complete separation is effected. This process is called **fractional distillation**, and may be repeated as often as we please with constantly increasing differentiation of the fractions.

An experimental illustration may be given by mixing 0.4 c.c. of benzene (b.-p. 80.4°) with 8 c.c. formic acid (b.-p. 100°) and 2 c.c. benzyl alcohol (b.-p. 206.5°) and boiling a part of the mixture in a test-tube with a small flame. The components come off in succession, and are recognized by the fact that the first and last burn with a luminous flame, while the flame of the second is non-luminous. By passing the vapors into a condenser, and using the method described above, a more or less complete separation can be made.

General Properties of Hydrocarbons. — All these substances are extremely indifferent in their chemical behavior. They have none of the properties of acids, bases, or salts. The halogens, notably chlorine and bromine, however, interact with them (see below). When burned they all produce carbon dioxide and water. When their vapors are passed through a white-hot tube they suffer decomposition into a mixture of hydrogen and hydrocarbons of smaller or larger (see Benzene) molecular weight.

Methane. — Methane, otherwise known as *marsh-gas*, is the chief component of natural gas. It rises to the surface when the bottoms of marshy pools are disturbed, and issues from seams in coal beds. In these two cases it results from the decomposition of vegetable matter in absence of air. When methane enters mines from a coal seam it is called "fire-damp" (Ger. *Dampf*, vapor), on account of the explosive nature of the mixture it forms with the air. The carbon dioxide formed by the explosion is called by the miners "choke-damp."

Methane may be made from inorganic materials by the action of

the great separation of free carbon which takes place temporarily during the combustion (*cf.* Flame), is highly luminous. It will be seen that in the formula but three of the valences of each carbon unit are occupied. As carbon is either bivalent or quadrivalent, we should expect that in this compound the combining capacity of the carbon would not be completely satisfied. We find this to be the case. Ethylene is easily reduced by nascent hydrogen (p. 423) to ethane, taking up two units of hydrogen in the process. When ethylene is passed through liquid bromine it is rapidly absorbed, and the bromine seems to increase in volume and finally loses all its color, leaving a transparent liquid having the composition $C_2H_4Br_2$, **ethylene bromide**. The second of the above graphic formulæ for ethylene is the one generally used. In spite of appearances, it is not intended to indicate that the two units of carbon are more forcibly held together than in other compounds (*cf.* p. 106). It simply chronicles the fact that one valence of each carbon unit is unoccupied.

Acetylene. — This substance, likewise a gas, is the first member of still another unsaturated, homologous series. Its formula C_2H_2 shows that its molecule lacks four of the hydrogen units necessary to the complete saturation which we find in ethane. Graphically its structure is usually represented thus: $H-C\equiv C-H$. This gas is formed in small quantities by direct union of carbon and hydrogen in the electric arc (p. 478). It is also produced when ethylene is passed through a heated tube: $C_2H_4 \rightarrow C_2H_2 + H_2$ (*cf.* Flame). When calcium carbide (p. 478) is thrown into water, violent effervescence occurs, the calcium carbide is disintegrated, a precipitate of calcium hydroxide is formed, and acetylene passes off as a gas:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2.$$

This action is like that of water on calcium phosphide (p. 461), calcium sulphide (p. 376), and magnesium nitride (p. 417).

Acetylene burns with a flame which is still more luminous than that of ethylene. Its most characteristic property is that when passed through an ammoniacal solution of a cuprous salt, it yields a red precipitate of a carbide of copper known as **copper acetylene**. The equation: $Cu_2(OH)_2 + C_2H_2 \rightarrow Cu_2C_2 + 2H_2O$, partially represents the change. This red precipitate, when dried, is extremely explosive, on account of the great amount of energy set free when it breaks up into

its constituents. Its formation is used as a test for acetylene in mixtures of gases.

Acetylene may be handled safely as a gas at the ordinary pressure, but when contained in cylinders at more than two atmospheres pressure it is readily exploded by any shock. This is due to the fact that it is an endothermal compound:

$$C_2H_2 \rightarrow 2C + H_2 + 53{,}200 \text{ calories.}$$

When used as an illuminant, it is developed in a suitable generator as it is needed. It begins visibly to decompose at 780°.

The unsaturated nature of this substance is shown by the avidity with which it unites with hydrogen and the halogens, forming saturated compounds.

Benzene. — Limits of space forbid the discussion of any of the other series of hydrocarbons. One of the most important has not been mentioned, however. It is that of which the first member is **benzene**, C_6H_6. More than half of the known compounds of carbon are derived from this substance. Phenol (*cf.* p. 441) C_6H_5OH is the fundamental alcohol of this set. Benzene is obtained from the products of the dry distillation of coal (*cf.* Coal gas), being formed, probably, from the acetylene which the decomposition of other hydrocarbons yields. At all events, when acetylene is passed through a heated tube some benzene is produced, $3C_2H_2 \rightarrow C_6H_6$, along with free carbon and hydrogen.

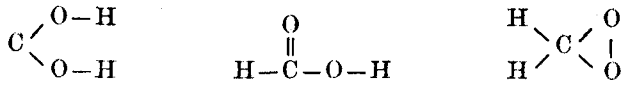
The Acids of Carbon.

Formic Acid. — The removal of water from formic acid produces carbon monoxide (p. 485). Although we cannot reverse the process and cause carbon monoxide to combine with water, we can make it unite with bases. By passing carbon monoxide over hot sodium hydroxide, we obtain sodium formate, from which formic acid may be liberated by double decomposition with another acid:

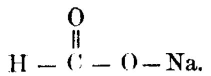
$$CO + NaOH \rightarrow CHO(ONa).$$

This acid is secreted by red ants, and is found in stinging nettles. It is a liquid boiling at 100.1° and freezing at 8.6°. Although one of the weaker acids, it is much more active than acetic acid. The molecule contains two atoms of hydrogen, but the acid is, in fact, monobasic.

The structural formula of the acid must take account of this fact. Three possibilities present themselves:



In the first and last the hydrogen units should behave alike. The second formula is the only one which expresses the replaceability of one unit and not of the other by a metal. Since the hydrogen in methane is not replaceable by metals (p. 493), we infer that the unit directly combined with carbon is the non-replaceable one. Sodium formate is therefore



Acetic Acid. — This acid is produced in the dry distillation of wood* (p. 476). Large quantities of it are manufactured from dilute alcohol. The liquid is allowed to flow in a slow stream through a barrel filled with shavings. Holes in the barrel provide for the access of air, and a bacterium with which the shavings are infected promotes that oxidation of the alcohol in which the change essentially consists:

$$C_2H_5OH + O_2 \rightarrow C_2H_3O(OH) + H_2O.$$

Oxygen alone does not affect alcohol in the cold. The bacterium (*B. aceti*, "mother-of-vinegar") assists this action, as lower organisms are found to assist many chemical actions, in a way which is not as yet thoroughly understood, and which may be described roughly as catalytic (see Fermentation, p. 501).

The dilute solution of acetic acid produced in this manner contains from five to thirteen per cent of acetic acid, and is known as **vinegar**. By fractional distillation the solution may be concentrated until a little water only remains, and finally, by freezing (*cf.* p. 294), the acetic acid may be crystallized out. Pure acetic acid, in consequence of its freezing readily in cold weather, is known as "glacial" acetic acid. It melts at 16.7° and boils at 118°.

Although four atoms of hydrogen are contained in its molecule, but one of these is replaceable by metals. This fact is recognized in the constitutional formula (p. 391) of the acid, $CH_3CO(OH)$. In this

* The dry distillation of bones (p. 455), on the other hand, and of animal matter (p. 417) in general, gives alkaline liquids, because of the ammonia that is formed.

acid a radical, methyl (CH_3-), takes the place of H in formic acid. The other organic acids similarly are related to formic acid and contain other organic radicals (see Palmitic acid). Thus the group $-\overset{O}{\overset{\|}{C}}-O-H$, called **carboxyl**, is contained in all carbon acids, and in each of them, as in formic acid, bears the replaceable hydrogen unit. The other three hydrogen units in acetic acid, however, are replaceable by chlorine, as is the case with the hydrogen units in hydrocarbons.

The above brief statements in regard to the mode of expressing the chemical properties of a substance by an elaborated formula bring out a tendency which prevails in the behavior of organic substances and is almost entirely lacking in inorganic chemistry. The units may be removed from the molecule of an organic substance one by one, and other units or groups may be substituted for them without disturbing the rest of the molecule. The changes take place, not as in the case of ionized substances, by the splitting of the molecule into two or more groups which act as wholes, but by the displacement of the units piecemeal and the introduction of new properties according to the nature of the groups introduced. Thus, if by any means we replace an atom of hydrogen by the organic radical $-\overset{O}{\overset{\|}{C}}-O-H$ the product is an acid. If we replace it simply by the group OH the product is an alcohol. Each substitution may take place repeatedly in a given molecule, so that di-basic or tri-basic acids, di-hydric or tri-hydric alcohols (see Glycerine), or substances which contain both OH and $-COOH$ in the same molecule (like lactic acid and tartaric acid), are formed. Other groups which may be introduced or removed are $-NH_2$, $-NO_2$, $-CN$, etc., each of which confers upon a substance the properties which go with the group, irrespective of the other features which the structure of the substance may already present.

Oxalic Acid. — This acid has the composition $H_2C_2O_4$, and is dibasic. Its calcium salt is the least soluble of the salts of calcium, and is found in many plants in the form of bundles of needle-shaped crystals. Potassium hydrogen oxalate is found in the juices of various species of *oxalis*. The acid may be made by oxidation of sugar with nitric acid.

Oxalic acid is commonly used in the form of the white crystalline hydrate, $H_2C_2O_4, 2H_2O$. When heated carefully it sublimes unchanged. Stronger heating decomposes it into carbon dioxide and formic acid, and the latter breaks up, in part, into water and carbon monoxide. In the presence of dehydrating agents like sulphuric acid, water and the two oxides of carbon alone are formed (p. 485).

Carbohydrates and Fermentation.

Carbohydrates. — The various kinds of sugar, starch, and cellulose form a closely related group of substances. As it happens that the proportion of hydrogen to oxygen in the composition of most of them is the same as that of these elements in water, they are known by the name of *carbohydrates*. None of these substances show any distinct evidence of ionization.

Dextrose, otherwise known as **glucose** or **grape-sugar**, is a white crystalline substance having the composition $C_6H_{12}O_6$. It is found dissolved in the juices of sweet fruits, such as grapes.

The most familiar sugar is **cane-sugar** $C_{12}H_{22}O_{11}$, which may form as much as 18 per cent by weight of the juices pressed from the sugar-cane, and sometimes reaches 15 per cent of the fluid material in the sugar-beet. It is prepared by boiling the juices with animal charcoal (p. 476), to remove the coloring matter which would otherwise give the sugar a brown tint. The liquid is then concentrated until crystals appear. The mother-liquor which no longer deposits crystals is known as *molasses*.

When a solution of cane-sugar is boiled with water containing a small amount of any acid, a slow hydrolysis of the sugar takes place, whereby two other sugars, namely, dextrose and levulose, are produced: $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$. The action of the acid is catalytic, and the rate of this more or less leisurely chemical change depends upon the concentration of the hydrogen ions. It therefore furnishes one means of comparing acids as regards their chemical activity, and has the special advantage that the acid is not consumed during the process (*cf.* p. 356), but remains of constant concentration throughout the whole time. This process, by which cane-sugar is decomposed, is spoken of as **inversion**, and the mixed product is called invert-sugar. The change can be produced, not alone by acids, but also by certain complex chemical compounds secreted by yeast (see below).

The relation of **starch** to the sugars is seen, not only in the formula $(C_6H_{10}O_5)_x$, but in the fact that by boiling starch with dilute acids, dextrose is formed along with other products of the hydrolysis. Commercial "glucose" is made by this process. Starch is an insoluble white substance which is found in the form of fine particles in the fruit and other parts of plants.

Cellulose has the same composition as starch. It forms the frame-

work of the cells of plants. In many cases it is overlaid with a considerable thickness of lignin, which in paper-making is removed by boiling the wood with sodium hydroxide or calcium bisulphite solution (p. 476). When the product has been washed thoroughly with water, almost pure cellulose remains. Matted cellulose in thin sheets forms the basis of paper, and filter paper contains nothing else (see under Aluminium sulphate). Other forms of pure cellulose are known as cotton, linen, and jute, according to their sources. Although the chemical composition of these varieties is identical, the physical properties vary considerably.

Fermentation. — This is the name given to a number of different chemical changes, brought about by catalytic action of complex chemical compounds secreted by living organisms. These compounds are called **enzymes**, and, in many cases, have been separated from the organisms by means of solvents. Their action must be regarded as catalytic, since small quantities of the active organisms or of the enzymes can produce very extensive chemical changes without themselves suffering alteration in the process.

The organisms may be divided into three classes, each secreting different enzymes which confine themselves for the most part to special kinds of chemical change. (1) The **molds**, when grown in sugar solution or beef extract, or other nutritive solutions, produce decompositions known collectively as putrefaction. (2) **Certain bacteria** promote the oxidation of alcohol to acetic acid (p. 498). Some also decompose sugar, furnishing butyric or lactic acid as one of the products. (3) The **yeasts** (*saccharomycetes*) flourish in solutions of some sugars, and decompose them into alcohol and carbon dioxide. This decomposition is known as alcoholic fermentation. These changes are usually brought about by actual introduction of the organism. In brewing, however, the enzyme itself, diastase, is employed to hydrolyze starch.

The juice of grapes when set aside at a suitable temperature soon begins to ferment, owing to the propagation in it of a yeast (*S. ellipsoideus*) which is found upon the skins of the grapes, and decomposes the sugar. While small quantities of a number of different compounds are formed, by far the greater part of the sugar is resolved quantitatively into alcohol and carbon dioxide: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$. The liquid effervesces, and the carbon dioxide escapes into the air. The **wine** is allowed to stand, after fermentation, until it has deposited a considerable crust of material known as argol, which consists mainly of

potassium-hydrogen tartrate ($KHC_4H_4O_6$, cream of tartar). The concentration of the sugar in the grape-juice being small, the quantity of alcohol contained in the product is not very great. By distillation of wine, a liquid containing a much larger proportion of alcohol is made, and is known as **brandy**. The special flavors of wines and brandies depend upon materials, other than sugar, originally contained in the fermented liquid, upon by-products of the fermentation, and upon materials which arise by slow chemical changes while the liquor is stored.

The preparation of **beer** involves a preliminary step, for the sugar needed for the fermentation is made from the starch contained in various kinds of grain, particularly barley. The conversion of starch into sugar is effected by the use of diastase, which is formed in considerable amounts in sprouting barley.* When the quantity of this unorganized ferment has reached a maximum, the barley is dried and crushed. The product, known as malt, is mixed in water with other grain which has not gone through this process, and the whole is slowly heated. During the heating, the diastase hydrolyzes the molecules of the starch, giving a sugar called maltose ($C_{12}H_{22}O_{11}$). The solution, after filtration and boiling, is cooled. It is then placed in the fermentation vats, and common yeast (*S. cerevisiæ*) is added. During the growth of this plant the maltose is decomposed, each molecule producing two molecules of dextrose, and the latter is broken up into alcohol and carbon dioxide according to the equation already given. Aside from the alcohol and carbon dioxide, considerable quantities of other substances extracted from the grain remain in the solution and form the so-called "extract," which varies in kind and quantity in different varieties of beer.

Whiskey is prepared in a somewhat similar fashion, although other sources of starch, such as rye and corn, may be used. The fermented *liquid contains but a small proportion of alcohol, and is distilled (rectified)*. The alcohol, being more volatile than water, tends to pass over first, and a product containing any desired proportion of it (see, however, below) can be made. Alcohol for technical or chemical use is made in the same way, potatoes sometimes being used as a source of the starch.

* In the digestion of bread, potatoes, and other food containing starch, the same office is performed by the saliva. Starch, being insoluble, could not be absorbed through the walls of the alimentary tract, while sugar is soluble and can be so absorbed. In a roughly similar way the albuminous parts of food are rendered soluble and capable of assimilation by the pepsin of the stomach, and the pancreatin of the large intestine, which convert them into peptones.

Alcohols, Esters, and Ethers.

Alcohols. —We have already seen that when wood is distilled, **methyl alcohol** is found in the fluid product. When purified this is a colorless liquid boiling at 66°. Its solution in water shows no evidence of ionization, although it would probably be safer to say that the ionization is so slight as to be imperceptible, than to say that the compound is not ionized at all. The formula (CH_3OH) makes it impossible to represent the structure of the substance in more than one way:

$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H-C-O-H} \\ | \\ \mathrm{H} \end{array}$$

All alcohols contain the group $\equiv C-O-H$ (*cf.* p. 499).

Common alcohol, **ethyl alcohol** C_2H_5OH, is formed in the fermentation of solutions of sugar by yeast (p. 501), and is separated from the water and the other products of fermentation by distillation. The product contains 95 per cent of alcohol and 5 per cent of water, and is applicable to most commercial uses. Absolute alcohol, entirely free from water, cannot be made by distillation alone (see below). The 95 per cent spirit is placed in vessels filled with quicklime, the latter interacts with water producing calcium hydroxide, and the clear liquid which is poured off is distilled once more. Pure alcohol boils at 78.3°.

Mixtures of two liquids, when distilled, behave in one of three ways. Two of these have been described already (p. 183), and alcohol (b.-p. 78.30°) and water (b.-p. 100°) illustrate the third. In this case the vapor tension of a certain mixture is higher than that of any other mixture and higher than that of either component separately. This special mixture has, therefore, a *lower* boiling-point than any other. In the present instance this mixture contains 95.57 per cent of alcohol and 4.43 per cent of water and boils at 78.15°. When the fermented liquid, with its large percentage of water, is distilled, the alcohol all tends to pass off first, in association with that part of the water required to constitute the mixture of minimum boiling-point. Repeated distillation simply eliminates more completely the excess of water beyond this amount (viz., 4.43 per cent), by leaving it in the residues.

Glycerine (p. 452) is an alcohol containing three hydroxyl groups, a trihydric alcohol.

Esters. — When an organic acid and an alcohol are mixed, a very slow chemical action takes place, which, being reversible, in no case reaches completion. With the simplest members of these groups, formic acid and methyl alcohol, for example, the change is:

$$HCOOH + HOCH_3 \rightleftarrows HCOOCH_3 + H_2O.$$

The product is known as **methyl formate**. The corresponding action between acetic acid and ethyl alcohol: $CH_3COOH + HOC_2H_5 \rightleftarrows CH_3CO OC_2H_5 + H_2O$, results in the formation of **ethyl acetate**. In this case, when equivalent quantities of the initial substances have been used without any solvent, and a condition of equilibrium has been reached, two-thirds of the material is found to have been transformed into ethyl acetate and water. If we start with the latter materials in pure form, the same equilibrium point is reached, and one-third of the material is converted into acetic acid and alcohol.

This action is a general one, and occurs between all alcohols and acids. The products are sometimes known as ethereal salts, because they result from the displacement of the hydrogen of an acid by a radical. This designation, however, is not very happy, since the products are not ionized and possess none of the properties of salts. The special name **esters**, therefore, has been given to them. The action is always extremely slow and never complete, but it may be hastened and carried to completion by the introduction of some substance capable of absorbing the water and so preventing the reversal. Concentrated sulphuric acid, for example, or anhydrous cupric sulphate, may be used.

Inorganic acids also interact with alcohol, giving esters. Thus, **nitroglycerine** (p. 452) is an ester, and should be called glyceryl trinitrate. The use of sulphuric acid to assist in the removal of the water is illustrated in the preparation of this substance. **Gun-cotton** (p. 441) is an ester of nitric acid also, for cellulose is a complex alcohol. **Ethyl sulphate** (p. 495) is an ester of sulphuric acid. In this case the action may be made complete by using sulphuric acid containing an amount of sulphur trioxide sufficient to combine with the water to be produced.

The above actions, in which an ester, like ethyl acetate, is formed, may be almost completely reversed if a sufficient amount of water is added (*cf.* p. 250). The hydrolysis of the ester is hastened by the presence of free acids in the water. This is owing to the catalytic action of the hydrogen ions, and the acceleration is proportional to the activity of the acid used. The acid, however, although it hastens the

action, does not carry it beyond the condition of equilibrium which it would eventually have reached with the same amount of water alone (*cf.* p. 237).

When esters are boiled with strong bases, such as sodium hydroxide solution, the salt of the acid and an alcohol are formed:

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + HOC_2H_5.$$

With more complex esters the sodium salts of the acids thus produced are known as **soaps**, and this general kind of action is called, therefore, **saponification** (Lat. *sapo*, soap). The speed with which it proceeds may be used as a means of measuring the activity of bases.

Soap. — Soap is prepared by the decomposition of fat. The latter substance is a mixture of several rather complex esters. In beef fat the chief esters present are tripalmitin, tristearin, and triolein.* It will be sufficient to illustrate the chemistry of the change by discussing the case of one of these substances. Tripalmitin is the glyceryl ester of palmitic acid. When fat is mixed with hot sodium hydroxide solution it first forms an emulsion† in which the fat is disseminated in minute droplets through the liquid. This is a result of surface tension. When the emulsion is boiled, the fat is slowly decomposed into sodium palmitate and glycerine. The change is precisely similar in plan to the simpler one just discussed:

$$\begin{array}{l} C_{15}H_{31}COO-C-H_2 \\ \qquad\qquad\quad | \\ C_{15}H_{31}COO-C-H \\ \qquad\qquad\quad | \\ C_{15}H_{31}COO-C-H_2 \end{array} + 3NaOH \rightarrow 3C_{15}H_{31}COONa + \begin{array}{l} HOCH_2 \\ \quad | \\ HOCH \\ \quad | \\ HOCH_2 \end{array}$$

Changes similar to this occur with the other two substances. The only difference is that the organic radical in the case of tristearin is $C_{17}H_{35}$, and in the case of triolein $C_{17}H_{33}$. Both products in each case are soluble in water, but when common salt is added to the solution the sodium salts of the organic acids are separated ("salted out," see Chap. xxxv) as a solid mass, which is known as soap. When potassium hydroxide takes the place of sodium hydroxide the mass is semi-fluid, and is known as soft soap.

* Butter fat contains in addition to the above a certain amount of tributyrin, in which the organic radical is C_3H_7. Olive oil consists mainly of tripalmitin and triolein.

† In the intestines the same office is performed by the gall, secreted by the liver, and so the fat is prepared for absorption into the system.

These complex esters, like the simpler ones, are decomposed also by water without the aid of a base, although much more slowly. By the use of superheated steam, however, rapid hydrolysis can be produced, and the products are the free organic acids and glycerine. The mixture of acids set free from fat by the action of steam is a solid, waxy mass, known as "stearin," and used in the manufacture of candles. The oleic acid, which is a liquid, is pressed out.

These acids, not being soluble in water, have no effect upon litmus; but the fact that they are acids may be recognized when it is found that they are converted into soluble salts by bases, such as sodium hydroxide:

$$C_{17}H_{35}COOH \uparrow + NaOH \rightleftarrows H_2O + C_{17}H_{35}COONa.$$

The cleansing power of soap solution seems to depend on the surface tension of the liquid rather than on any chemical action.

The components of soap, like other salts, are highly ionized in solution, and show all the properties of ionogens. When soap is dissolved in hard water (*cf.* p. 113), a white, flocculent precipitate is formed, which coagulates upon the sides of the vessel. This is a mixture of the calcium salts formed by union of the proper ions. For example, the sodium palmitate is changed as follows:

$$2C_{15}H_{31}COONa + CaSO_4 \rightarrow (C_{15}H_{31}COO)_2Ca \downarrow + Na_2SO_4.$$

Most of the salts of these acids, with the exception of those of potassium and sodium, are insoluble in water.

Drying Oils. — The oils commonly used as "dryers" for mixing with varnish and paint and in making linoleum, such as linseed oil, hemp oil, poppy oil, and nut oil, contain esters of acids with unsaturated radicals. One of the constituents, for example, is the glyceryl ester of linoleic acid. The formula of this acid is $C_{17}H_{31}COOH$. It contains four hydrogen atoms less than the corresponding saturated acid (stearic acid). These oils, especially after having been recently heated, alone or with catalytic agents like lead oxide and manganese dioxide, absorb oxygen rapidly from the air, and become solid. They do not dry, in the ordinary sense, by evaporation.

Ether. — When two molecules of an alcohol lose one molecule of water, an ether is produced:

$$2CH_3OH \rightarrow (CH_3)_2O + H_2O.$$

Thus, methyl alcohol gives **methyl ether**, and ethyl alcohol, **ethyl** or common **ether**. The action is most easily carried out by two steps. In making common ether, ethyl alcohol acts upon sulphuric acid, giving ethyl sulphate (p. 495); and the latter, when warmed gently with excess of alcohol, gives ethyl ether:

$$C_2H_5HSO_4 + C_2H_5OH \rightarrow (C_2H_5)_2O \uparrow + H_2SO_4.$$

The ether escapes as vapor and is condensed.

Ethyl ether is a volatile liquid boiling at 34.6°. It is largely used as a solvent for iodine, fats, and other substances not readily soluble in water, and as an anæsthetic.

CYANOGEN.

Cyanogen. — This compound is formed in small amount when a discharge of electricity takes place between carbon poles in an atmosphere of nitrogen (*cf.* p. 416). Cyanogen, being an endothermal substance, is more easily made as one product in an exothermal action (p. 301). It is prepared by allowing a solution of cupric sulphate to trickle into a warm solution of potassium cyanide. The cupric cyanide, at first precipitated, quickly decomposes, giving cuprous cyanide and cyanogen:

$$2KNC + CuSO_4 \rightarrow Cu(NC)_2 \downarrow + K_2SO_4,$$
$$2Cu(NC)_2 \rightarrow 2CuNC + C_2N_2 \uparrow.$$

Cyanogen is a very poisonous gas with a characteristic, faint odor.

Hydrocyanic Acid. — This acid, called also prussic acid, has the formula $H-N=C$, and is most easily made by the action of an acid upon a cyanide (see Potassium cyanide) followed by distillation. It is a colorless liquid boiling at 26.5°. It has an odor like that of bitter almonds, and is highly poisonous. In aqueous solution it is an extremely feeble acid, and is hardly ionized at all. In consequence of this, potassium cyanide is markedly hydrolyzed by water, and its aqueous solution is strongly alkaline. The behavior of hydrocyanic acid shows it to be an unsaturated body, a fact which is taken account of in the above formula, and illustrated in the two following paragraphs.

Cyanates. — When potassium cyanide is fused and stirred with an easily reducible oxide, like lead oxide (PbO), the metal (for example,

the lead) collects at the bottom of the iron crucible in molten form, and potassium cyanate is produced:

$$KNC + PbO \rightarrow KNCO + Pb.$$

Cyanic acid is itself very unstable. Ammonium cyanate is chiefly remarkable for its transformation into urea (p. 488).

Thiocyanates. — When potassium cyanide in aqueous solution is boiled with sulphur or with a polysulphide (p. 376), it is converted into potassium thiocyanate, KCNS. This salt is used in testing for ferric ions on account of the deep-red color of ferric thiocyanate (*cf.* p. 250). The ammonium salt undergoes at 170° a transformation parallel to that of ammonium cyanate, thiocarbamide (sulpho-urea) being formed.

Exercises. — 1. Make the graphic formulæ of hexane (p. 491), methyl acetate (p. 499), ethyl formate, ethylene bromide (p. 496), oxalic acid (p. 499), ethyl ether (p. 507).

2. Make equations for the formation of aluminium carbide (p. 478), the hydrolysis of starch to maltose (p. 502), the saponification of triolein (p. 505).

3. Name the radicals: C_5H_{11}, C_5H_{10}, C_5H_9, $C_{16}H_{18}$, and the substances $C_5H_{11}Cl$, $C_5H_{11}OH$, $(C_5H_{11})_2O$, $C_5H_{11}HSO_4$.

4. Is the hydrocarbon radical of oleic acid (p. 505) saturated, or not?

5. Prepare a **summary** of the various statements that have been made in the text about **catalysis** (*e.g.* pp. 75, 109, 111, 170, 175, 189, 237, 380, 396, 399, 423, 484), and illustrate fully.

CHAPTER XXX

FLAME

Meaning of the Term. — In the combustion of charcoal there is hardly any flame, for the light emanates almost entirely from the incandescent, massive solid. When two gases are mixed and set on fire, a sort of flame passes through the mixture, but this can hardly be accounted a flame, in the ordinary sense, either. The rapid movement of the flash, and the explosion which accompanies it, are in a manner the precise opposite of the quiet combustion which is characteristic of flames.

With illuminating-gas the production of its very characteristic flame is due to the chemical union of a stream of one kind of gas in an atmosphere of another. The flame is made up of the heated matter where the two gases meet. In the case of a burning candle, one of the bodies appears to be a solid, but a closer scrutiny of the phenomenon shows that the solid does not burn directly. A combustible gas is manufactured continuously by the heat of the combustion and rises from the wick. The introduction of a narrow tube into the interior of the flame enables us to draw off a stream of this gas and to ignite it at a remote point. Thus, **a flame is a phenomenon produced at the surface where two gases meet and undergo combination with the evolution of heat and, sometimes, light.**

In the chemical point of view, it is a matter of indifference whether the gas outside the flame contains oxygen, and the gas inside consists of substances ordinarily known as combustibles, or whether this order is reversed. In an atmosphere of ordinary illuminating-gas, the flame must be fed with air. This condition is easily realized (Fig. 93). The lamp-chimney is closed at the top until it has become filled with illuminating-gas. After the lapse of a few minutes this can be ignited as it issues from the bottom of the wide, straight tube which projects from the interior. When the hole in the cover of the lamp-chimney is then opened, the upward draft causes the flame of the burning gas to recede up the tube, and there results a flame fed by air and burning in coal-gas. In an atmosphere of this kind, materials playing the part of a candle burning in air would have to be substances which, under the

influence of the heat of combustion, give off oxygen. Strongly heated potassium chlorate, for example, appears to burn continuously in such an atmosphere when lowered into it in a deflagrating spoon.

Luminous Flames. — The flame of hydrogen, under ordinary circumstances, is almost invisible, nearly all the energy of the combustion being devoted to the production of heat. A part of this, however, may be transformed into light by the suspension of a suitable solid body, such as a platinum wire, in the flame. The holding of a piece of quicklime in an oxyhydrogen flame (*cf.* p. 109) is a practical illustration of this method of securing luminosity. In general, luminosity may be produced by the presence of some incandescent solid.

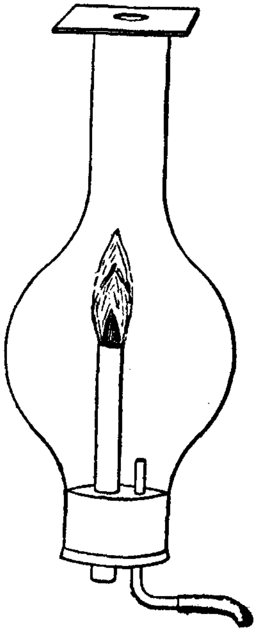


FIG. 93.

In the Welsbach lamp the flame itself is non-luminous, and, but for the mantle, would be identical with the ordinary Bunsen flame. The mantle which hangs in the flame, however, by its incandescence, furnishes the light. This mantle is composed of a mixture of 99 per cent thorium dioxide (ThO_2) and one per cent cerium dioxide (CeO_2). While many oxides would give out a white light and could be obtained much more cheaply than these, they have not sufficient coherence to make their use practicable. It is worth noting that any appreciable variation from the above proportions, by the introduction of either more or less cerium oxide, produces a marked diminution in the intensity and whiteness of the light (see, also, under Thorium).

In cases of brilliant combustion, as of magnesium ribbon or phosphorus, a solid body is formed whose incandescence accounts for the light. The flame of ordinary illuminating-gas does not at first sight appear to give evidence of the presence of any solid body. But if a cold evaporating dish is held in the flame for a moment, a thick deposit of finely divided carbon (soot) is formed, and we at once realize that the light is due to the glow of these particles in a mass of intensely hot gas. Carbon is, indeed, an extremely combustible substance, and

is eventually entirely consumed. But a fresh supply is continually being generated in the interior of the flame, while the oxygen with which it is to unite is outside the flame altogether. Thus the carbon particles persist until, drifting with the spreading gas, they reach the periphery of the flame.

It cannot be said that no flames are luminous unless a solid body is contained in them. When compressed hydrogen is burned in an atmosphere of oxygen under pressure, the light given out by the flame is much greater, and, in general, illuminating power seems to be heightened by increase in the density of the gas. In special cases, also, such as the explosion of a mixture of nitric oxide with carbon bisulphide vapor, a flame which has considerable illuminating power is produced, although the density of the gases is low and solids are lacking.

The Bunsen Flame. — In the burner devised by Robert Bunsen, a jet of ordinary illuminating-gas is projected from a narrow opening into a wider tube. In this tube it becomes mixed with air, drawn in through openings whose dimensions can be altered by means of a perforated ring. When the supply of air is sufficient, the flame becomes non-luminous. With a somewhat different construction, and the use of a bellows to force a larger proportion of air into the gas, a still hotter flame can be produced. The instrument in this case is known as a blast-lamp. The high temperature of the Bunsen flame is not difficult to account for. It will be seen at once, on handling the burner, that the flame diminishes to one-half or one-third of its previous size when air is admitted. Since the same amount of gas is burning in both cases, and the products in both cases are ultimately alike, the total amounts of heat produced must in both cases be the same. This statement may safely be made, since experiment shows that when chemical substances pass from one condition to another, the amount of heat evolved is the same whatever intermediate steps may be taken or omitted (*cf.* p. 78). The production of an equal amount of heat in a smaller flame necessarily causes this to have a higher average temperature. It will be noted that it does not follow from this that the temperature is higher in every part of the non-luminous flame than in the corresponding locality in the luminous flame. We shall see later, indeed, that this is not the case.

It is instructive to note the effect of forcing in larger and larger proportions of air into the Bunsen flame. The flame at the top of the tube continually diminishes in size, even after it has become non-

luminous. Finally, a point is reached at which the flame is so unstable that the smallest further increase in the supply of air causes it to descend into the tube. The mixture of illuminating-gas and air in the tube of a Bunsen burner is an explosive one, and the explosion-flame will proceed through it with greater rapidity, the more nearly the quantity of air approaches that required for complete combustion. When the speed with which the explosion-flame would move, equals that with which the stream of the mixed gases is coming upward through the tube, the flame reaches the unstable condition just mentioned. Any increase in the proportion of air raises the speed with which the explosion can travel, and the flame is thus able to proceed down the tube against the stream of gas. This phenomenon is frequently noticed in the Bunsen burner, when the holes admitting the air are too large, or a draft momentarily causes an increase in the supply of air. The flame "strikes back," and thereafter continues to burn at the bottom of the tube.

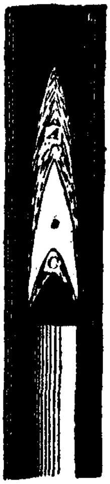


FIG. 94.

Structure of the Bunsen Flame. — When an exceedingly small luminous flame is examined, the various parts of which it consists may easily be made out. In the interior there is a dark cone which is composed of illuminating-gas and air, and in it no combustion is taking place. A match-head may be held here for some time without being set on fire. This is therefore not properly a part of the flame. Outside this is a vivid blue layer (*C*, Fig. 94) which is best seen in the lower part of the flame, but extends beneath the luminous sheath, and covers the dark inner cone completely. Outside the blue flame, and covering the greater part of it, is the cone-shaped luminous portion (*B*). Over all is an invisible mantle of non-luminous flame (*A*), which becomes visible when the light from the luminous part is purposely obstructed. In the luminous gas-flame, therefore, there are four regions, if we count the inner cone of gas. The difference between this and the non-luminous Bunsen flame is that in the latter the luminous region is omitted, and the inner, dark cone, the blue sheath, and the outer mantle, are the only parts which can be distinguished. We shall see that in these different regions the chemical changes taking place are different.

Composition of Illuminating-Gas. — Before considering the chemistry of the gas-flame, it is necessary to know what substances are burning. The illuminating-gas in Europe, and in many of the smaller cities of the United States, is usually coal-gas, while in the larger cities of America it is almost always made from water-gas. The former is obtained by the destructive distillation of soft coal, and is freed from ammonia (*cf.* p. 418) and tar by washing and cooling, and from hydrogen sulphide and carbon dioxide by passage through layers of slaked lime. The water-gas, made by the action of steam upon anthracite or coke, being composed of carbon monoxide and hydrogen (*cf.* p. 485), has no illuminating power. It is therefore "carburetted," that is, mixed with hydrocarbons, by passage through a cylindrical structure filled with white-hot firebrick, upon which falls a small stream of high-boiling petroleum. The relatively involatile hydrocarbons of which the oil is composed are thus decomposed ("cracked"), and gaseous substances of high illuminating power are produced. The following table shows the composition of each of these kinds of gas, together with that of oil-gas (Pintsch's), which is composed entirely of the products from "cracking" oil :

Components.	Coal-Gas.	Water-Gas.	Oil-Gas.
Illuminants	5.0	16.6	45.0
Heating gases:			
Methane	34.5	19.8	38.8
Hydrogen . . .	49.0	32.1	14.6
Carbon monoxide .	7.2	26.1	. . .
Impurities:			
Nitrogen	3.2	2.4	1.1
Carbon dioxide . .	1.1	3.0	. . .
Candle power . . .	17.5	25.0	65.0

These are average numbers, and considerable variations from these proportions are often met with. The illuminants are unsaturated hydrocarbons, such as ethylene, acetylene, and benzene, and the value of the gas for illuminating purposes depends on the amount of these particular components.

Chemical Changes Taking Place in the Bunsen Flame. — The study of the chemical changes taking place in the Bunsen flame,

particularly with the object of explaining (1) the luminosity of the flame of the pure gas, and (2) the non-luminosity of that produced by the same gas when it is mixed with air, has been the subject of many elaborate investigations. The questions are: Why is carbon liberated in the former case, and why is it not liberated in the latter? Let us consider these questions in order.

1. The first suggestion of an explanation of the presence of free carbon in the luminous flame was that the hydrocarbons contained in the gas underwent a selective combustion. This was supposed to take place in such a way that the hydrogen was first burned out of the molecules by the oxygen, which, by diffusion, had penetrated farthest into the flame. The carbon had, therefore, to remain free until all the hydrogen was satisfied, and until the former had drifted into a region in which a more liberal supply of oxygen was obtainable. Thus the carbon was rendered incandescent by the heat of combustion of the hydrogen. This hastily formed theory is founded upon ill-considered premises, and is not supported by experiment. It is based upon the familiar fact that hydrogen gas burns more easily than solid charcoal. *Such a comparison, however, is not applicable to the case of the combustion* of a gaseous hydrocarbon, for in such a substance both of the elements are in a gaseous condition, and the inferior combustibility of charcoal is due, not to an inferior power of uniting with oxygen, but to the fact that, since it is a solid, the oxygen finds access to it only with difficulty.

The question could manifestly be placed beyond dispute if it were found possible to determine exactly the nature of the change which passage through the inner, blue zone of the flame produced. If, for example, gases could be extracted by means of a tube from the region just outside this zone, and it were found that all the hydrogen had been converted into water while the carbon had not yet reached the stage of carbon dioxide, this theory would be confirmed. It was found impossible, however, to perform the experiment in this fashion, on account of the disturbing influence of the currents produced by the withdrawal of the stream of gas. An apparatus devised by Smithells, however, furnished an ingenious means of securing the interconal gas, alone and in any quantity. The air and combustible gas are admitted in proportions which can be varied, and the mixture burns at the top of the wider tube (Fig. 95). As the quantity of air is increased, however, the speed with which an explosion-flame would pass through it becomes greater, and finally the inner cone passes down and rests upon the

mouth of the narrow tube through which the mixture of gases is issuing more rapidly. A preliminary combustion takes place in the blue cone, while the final conversion of the whole material into carbon dioxide and water is completed in the outer mantle. This remains at the top of the wider tube, where alone the necessary air can be obtained. By means of a side-tube (not shown) fused into the wider tube, the gases which have traversed the inner cone and undergone chemical change in it can be extracted and subjected to examination.

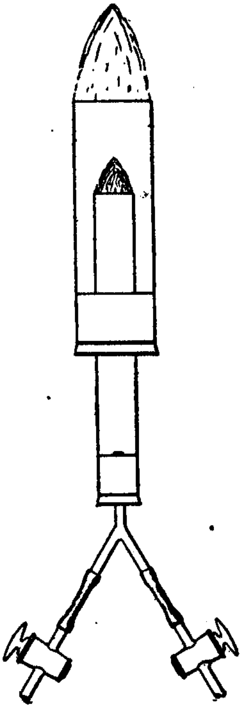


FIG. 95.

Now it was found that hardly any of the hydrogen had been burned by the blue cone, while all of the carbon had reached the stage of carbon monoxide. This was the case, not only with illuminating-gas, which initially contains much free hydrogen, but also when the flame was fed with *pure methane.* The greater part of the hydrogen of the latter was set free, and was found uncombined in the interconal gas. It is evident, therefore, that when a hydrocarbon undergoes partial combustion the *carbon is first attacked* and the burning of the hydrogen is postponed until a sufficient supply of oxygen becomes available.

We may safely infer, therefore, that since in the luminous flame a portion at least of the carbon remains for a time uncombined, the hydrogen must *a fortiori* have survived combustion also. The luminous cone must contain a mixture of free hydrogen and free carbon.

The production of this mixture can be explained in only one way, namely, by the *dissociation* of the hydrocarbons concerned, of which ethylene is the most important. Now we have seen (pp. 496 and 497) that, when heated, ethylene dissociates, giving acetylene, and acetylene gives carbon and hydrogen. Hence this stochastic hypothesis is highly probable. It only remains to be shown that acetylene is actually formed as an intermediate substance. Evidence of this is obtained in two ways. It is found that when the Bunsen flame "strikes back," and the combustion of the gases is rendered incomplete by the contact of the flame with

the cold tube, a large amount of acetylene is formed. Again, when the gases surrounding the flame of air burning in illuminating-gas (p. 509) are withdrawn by means of a pump and caused to pass through an ammoniacal solution of cuprous chloride (Fig. 96), large quantities of copper acetylene are formed.

The conception that when hydrocarbons burn, they first undergo dissociation, and then union with oxygen, is in harmony with what we have observed also in the case of the combustion of hydrogen sulphide, where the presence of free sulphur and free hydrogen in the interior of the flame was demonstrated (p. 378).

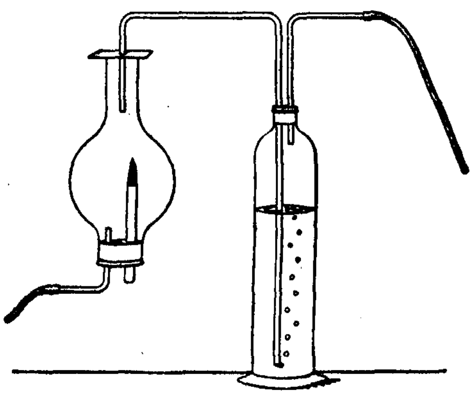


FIG. 96.

2. The influence of the air admitted to the Bunsen burner, in interfering with this dissociation in such a way as to destroy all luminosity, is the most difficult point to explain. The effect is frequently attributed to the oxygen which the air contains. This view, however, is seriously weakened by a consideration of the undoubted fact that oxygen is not required. Carbon dioxide and steam are equally efficient when introduced instead of air. Even nitrogen, which cannot possibly be suspected of furnishing any oxygen, likewise destroys the luminosity. Lewes has shown that 0.5 volumes of oxygen in 1 volume of coal-gas destroy the luminosity. But 2.30 volumes of nitrogen or 2.27 volumes of air accomplish the same result. Thus the efficiency of air is not much greater than that of nitrogen, in spite of the fact that one-fifth of the former is oxygen.

It is evident that the effect is due, in part at least, to the dilution with *cold* gas. This is confirmed by the observation that a cold platinum dish held in a small luminous flame is similarly destructive of the luminosity. Comparison of the temperatures of the inner sheaths of the luminous and non-luminous flames shows that the temperature of the latter is markedly lower. If the tube of the Bunsen burner is heated so that the mixed gases are considerably raised in temperature

before reaching the non-luminous flame, the latter becomes luminous. It is probable, therefore, that the cold gas lowers the temperature of the inner flame, and at the same time the dilution diminishes the speed of dissociation (Lewes). Even if the temperature is not reduced below that at which dissociation of the ethylene can occur, yet the dilution and cooling together prevent that sharp dissociation at this particular point which is necessary for the production of the great excess of free carbon needed to furnish the light.

Exercises. — 1. In what way will calcium hydroxide remove hydrogen sulphide from coal-gas (p. 513)?

2. Make a section showing the shape of the flame produced by burning hydrogen gas when the latter issues from a circular opening.

CHAPTER XXXI

SILICON AND BORON

IN respect to chemical relations there is a close resemblance between silicon and carbon. The former element gives no monoxide, however, and is quadrivalent in all its compounds. In chemical character it is strictly non-metallic.

Occurrence. — Silicon, unlike carbon, is not found in the free condition. In combination it is the most plentiful element after oxygen, and constitutes more than one-quarter of the crust of the earth. The oxide is silica or sand (SiO_2), and this oxide and its compounds are components of many rocks. In the inorganic world silicon is the characteristic element to almost as great an extent as is carbon in the organic realm.

Preparation. — When finely powdered magnesium and sand are mixed, and one part of the mass is heated, a violent action spreads rapidly through the whole:

$$2Mg + SiO_2 \rightarrow Si + 2MgO.$$

At the same time, and especially if excess of the metal is used, some magnesium silicide Mg_2Si is formed also. The mixture is treated with a dilute acid which decomposes the magnesium oxide and the silicide, and leaves the silicon alone undissolved. A simpler method, although one using less common materials, is to pass the vapor of silicon tetrachloride over heated sodium. The mixture of common salt and silicon which remains in the tube can be separated by washing with water. Both of these methods give amorphous silicon in the state of fine powder.

When amorphous silicon is dissolved in molten zinc, the mass, after solidification, is found to contain crystalline silicon. This form may be made in one operation, by heating three parts of potassium fluosilicate K_2SiF_6 with one part of sodium and four parts of zinc in a closed crucible. The sodium displaces the silicon and combines with the fluorine, while the zinc acts as a solvent as before. The zinc is removed by the action of a dilute acid, the silicon remaining unaffected.

Properties. — **Amorphous silicon** is a brown powder. It unites with fluorine at the ordinary temperature, with chlorine at 430°, with bromine at 500°, with oxygen at 400°, with sulphur at 600°, with nitrogen at about 1000°, and with carbon and boron at temperatures attainable only in the electric furnace. It is slowly oxidized by *aqua regia* to silicic acid, and is dissolved by a mixture of hydrofluoric acid and nitric acid, giving the fluoride.

Crystallized silicon consists of black needles belonging to the hexagonal system, and is less active than the other variety. It oxidizes superficially at 400°, and the dioxide formed on the surface hinders further action. With chlorine and fluorine it unites easily when heated. Gaseous hydrogen fluoride interacts violently with it at a high temperature, heat and light are given out, and silicon tetrafluoride and hydrogen are formed. It is slowly attacked by hydrofluoric acid mixed with nitric acid, but not by any others of the oxygen acids.

Both kinds of silicon act with fair speed upon boiling solutions of potassium or sodium hydroxide (*cf.* p. 99), the metasilicate being formed:

$$Si + 2KOH + H_2O \rightarrow K_2SiO_3 + 2H_2.$$

Silicon seems to be more active than carbon, for, when it is heated with fused potassium carbonate, potassium silicate is formed and carbon is liberated. Both kinds of silicon differ from carbon in being fusible at a very high temperature. The product is crystallized silicon.

Silicon Hydride. — Silicon differs from carbon in giving only two well-defined compounds with hydrogen. The chief one may be liberated as a gas by the action of hydrochloric acid upon magnesium silicide:

$$Mg_2Si + 4HCl \rightarrow 2MgCl_2 + SiH_4.$$

The action is similar to that by which hydrogen sulphide is made. Since the magnesium silicide always contains free magnesium, hydrogen is liberated at the same time. The gases may be separated by passage through a tube surrounded by liquid air. The silicon hydride is reduced to liquid form, while the hydrogen passes on. The mixture with hydrogen is spontaneously inflammable. The pure gas becomes so only when its pressure is reduced. In the air, however, it is easily inflammable, by contact with a warm body. When heated, it decomposes into its constituents.

Carbide of Silicon. — This compound is manufactured for use as an abrasive, and is sold under the name of *carborundum*. A mixture of quartz-sand, coke, and common salt is heated to about 3500° in the electric furnace:

$$SiO_2 + 3C \rightarrow SiC + 2CO.$$

The materials are piled upon an oblong base provided with vertical walls at the ends, through which the terminals project. A long ridge of loosely packed coke furnishes an imperfect conductor of high resistance between the terminals. The above mixture is heaped on each side of and above this, as well as below it. The coke becomes white-hot when the current is turned on, and the heat radiating from this core brings about a change, in the above sense, which affects the whole mass more or less completely.

Silicon carbide when pure is composed of transparent, colorless, hexagonal plates. Ordinarily the crystals are brown or black. It stands next to the diamond and carbide of boron in hardness. It is not oxidized by the air even at a white heat, being protected by the layer of silica first formed. Carborundum is not affected by water or acids, but is decomposed by alkalies. It is used in making machinery for polishing hard rock, such as granite, and is employed also for protecting the walls of puddling furnaces (*q.v.*), and in other ways in the steel industry.

Silicon Tetrachloride. — This compound is made by direct union of the free elements. It is more conveniently prepared by passing chlorine over a strongly heated mixture of silicon dioxide and carbon. The gaseous products enter a condenser in which the tetrachloride assumes the liquid form:

$$2Cl_2 + SiO_2 + 2C \rightarrow SiCl_4 + 2CO.$$

Chlorine is unable to displace oxygen from combination with silicon, and has, therefore, when alone, no effect upon sand. In the above action, therefore, the carbon is used to secure the oxygen while the chlorine combines with the silicon. This kind of interaction is in some degree different from any which we have hitherto encountered. It bears no special name, but the principle underlying it is very commonly employed (see, *e.g.*, Chlorides of boron and aluminium).

Silicon tetrachloride is a colorless liquid (b.-p. 59°) which fumes

strongly in moist air, giving silicic acid. It acts violently upon cold water, and in this respect differs from carbon tetrachloride:

$$SiCl_4 + 4H_2O \rightarrow 4HCl + Si(OH)_4.$$

The silicic acid (*q.v.*) which is formed soon appears as a gelatinous precipitate.

When silicon is heated in a stream of dry hydrogen chloride, a mixture of silicon tetrachloride and silico-chloroform $SiHCl_3$ is produced. The latter is a volatile liquid boiling at 34°.

Silicon Tetrafluoride. — When strong hydrofluoric acid acts upon sand, this gas is liberated:

$$SiO_2 + 4HF \rightarrow 2H_2O + SiF_4.$$

Since the water interacts with the tetrafluoride (see below), the latter is usually made by the use of powdered calcium fluoride and excess of sulphuric acid. In this way the hydrogen fluoride is generated in contact with the sand, and at the same time the sulphuric acid takes possession of the water. Hydrofluoric acid acts in a corresponding way upon all silicates (*q.v.*), whether these are minerals or are artificial silicates like glass (*cf.* p. 243).

Silicon tetrafluoride is a gas which becomes solid, without liquefying (*cf.* p. 463), when cooled to −102°. It fumes strongly in moist air, and acts vigorously upon water. This interaction is different from that of the tetrachloride, because the excess of the tetrafluoride forms a complex compound with the hydrofluoric acid:

$$SiF_4 + 4H_2O \rightarrow Si(OH)_4 \, (+ \, 4HF) \qquad (1)$$
$$(4HF) + 2SiF_4 \rightarrow 2H_2SiF_6 \qquad (2)$$
$$\overline{3SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 2H_2SiF_6}$$

The silicic acid is precipitated in the water, and may be separated by filtration, leaving a solution of hydrofluosilicic acid.

Hydrofluosilicic Acid. — This acid is stable only in solution. When the water is removed by evaporation, silicon tetrafluoride is given off, while most of the hydrogen fluoride remains to the last. Its salts are decomposed in a corresponding way when they are heated. This acid is used in analysis chiefly because its potassium and sodium salts are amongst the few salts of these metals which are relatively

insoluble in water. The barium salt is also insoluble, but most of the salts of the heavy metals are soluble.

Silicon Dioxide. — This substance may be made in the form of a fine white powder by heating precipitated silicic acid. It is found in many different forms in nature. In large, transparent, six-sided prisms with pyramidal ends it is known as **quartz** or **rock crystal**. When colored by manganese and iron it is called **amethyst**, when by organic matter, **smoky quartz**. A special arrangement of the structure gives **cat's eye**. Amorphous forms of the same material, often colored brown or red with ferric oxide, are **agate**, **jasper**, and **onyx**, the last much used in making cameos. **Infusorial** or diatomaceous **earth** is composed of the tests of minute organisms. Slightly hydrated forms of silica are the **opal** and **flint**. A crystalline variety belonging to the hexagonal system, but showing entirely different crystalline forms, occurs occasionally in minute crystals, and is called **tridymite**.

Silicon dioxide, although differing profoundly from carbon dioxide in its physical nature, nevertheless behaves like the latter chemically. Thus, when boiled with potassium hydroxide solution (*cf.* p. 482), it forms potassium orthosilicate:

$$SiO_2 + 4KOH \rightarrow K_4SiO_4 + 2H_2O.$$

The salt is left as a gelatinous solid ("soluble glass") when the water is evaporated. The silicates of potassium and sodium may also be obtained by boiling sand with the carbonates of these metals, carbon dioxide being displaced. They are produced more rapidly, however, as metasilicates (see below), by fusing the sand with the alkali carbonates:

$$SiO_2 + K_2CO_3 \rightarrow K_2SiO_3 + CO_2.$$

Silica is found in the hard parts of straw, of some species of horsetail (*equisetum*), and of bamboo. In the form of whetstones it is used for grinding. The clear crystals are employed in making spectacles and optical instruments. Pure sand is used in glass manufacture (*q.v.*). Infusorial earth, on account of the tubular form of many of the minute structures of which it is composed, can absorb three times its own weight of nitroglycerine, and is therefore employed in making dynamite. Recently, small pieces of chemical apparatus have been manufactured by fusing quartz in the oxyhydrogen flame. The material is very difficult to work, on account of its infusibility; but owing

to the low coefficient of expansion of silica, the vessels fashioned out of it can be heated or cooled as suddenly as we choose, without risk of fracture.

Silicic Acid. — When acids are added to a solution of sodium silicate, silicic acid is set free. After a little delay it usually appears as a gelatinous precipitate. When, however, the silicate is poured into strong hydrochloric acid, no precipitation occurs. The silicic acid remains in **colloidal solution** (see below). The acid before precipitation is supposed to be orthosilicic acid:

$$Na_4SiO_4 + 4HCl \rightarrow 4NaCl + Si(OH)_4,$$
$$Na_2SiO_3 + 2HCl + H_2O \rightarrow 2NaCl + Si(OH)_4,$$

but the gelatinous precipitate when it has been dried contains a smaller proportion of the elements of water. There seem to be no definite stages, indicating the existence of various acids, such as we observe with phosphoric acid. We should expect the vapor tension of the water to decrease by steps, each of which should correspond to some acid of a particular degree of hydration (*cf.* p. 122), but nothing of the sort is observed. The final product of drying is the dioxide. A *jelly* of the kind described above is called a **hydrogele**. A *solution* such as that containing dissolved silicic acid is called a **hydrosole**.

Silicic acid is a very feeble acid, and, therefore, gives no salt with ammonium hydroxide. For the same reason silicic acid can be completely displaced from its salts, even by so weak an acid as carbonic acid. Since the water in some geyser regions contains alkali silicates, the action of the carbon dioxide in the air causes deposition of silica round the places where the water issues from the ground. This form is known as **silicious sinter**. Striking scenic effects, as in the white and pink terraces of New Zealand, are sometimes produced by this method of deposition.

Colloidal Solution. — Silicic acid in colloidal solution can be separated from the other dissolved substances by a method discovered by Graham and called **dialysis**. The solution is placed in a vessel whose bottom is composed of vegetable parchment, or some animal membrane, and the whole is hung in a vessel of water. Salts which may be present pass slowly through the membrane into the water outside, and, when the latter is frequently changed, all of the material of this class in the solution may finally be removed.

The silicic acid, however, remains confined in the cell. **Substances** possessing the ability to pass through a membrane are usually crystalline, and in the present connection are therefore called **crystalloids**. On the other hand, materials of a gluey nature are unable to traverse the partition, and are named **colloids**. This behavior must not be confused with that in which a semi-permeable membrane (p. 284) is in question. In the latter case all dissolved substances are equally unable to penetrate the membrane.

A pure aqueous solution of a colloid lacks the properties characteristic of solutions. It boils and freezes at the same temperature as the pure solvent, and independent evidence shows that, although in too fine a state of division to be retained by a filter paper, the colloid is nevertheless simply suspended in the liquid.

Colloidal solutions of other substances which are insoluble in water, such as ferric hydroxide, aluminium hydroxide, and starch, and even of metals like gold, silver, and platinum, can likewise be made.

Silicates. — While, in the absence of definite knowledge, silicic acid is presumed to be the ortho-acid $Si(OH)_4$, and no other silicic acids have been made, the salts are most easily classified by imagining them to be derived from various acids representing different degrees of hydration of the dioxide, or, to put it the other way, different degrees of dehydration of the ortho-acid. The following equations show the relation of the ortho-acid to some of the silicic acids whose salts are most commonly found amongst minerals:

$$H_4SiO_4 - H_2O \rightarrow H_2SiO_3 \quad \text{Metasilicic acid.}$$
$$\left.\begin{array}{l} 2H_4SiO_4 - H_2O \rightarrow H_6Si_2O_7 \\ 2H_4SiO_4 - 3H_2O \rightarrow H_2Si_2O_5 \end{array}\right\} \text{Disilicic acids.}$$
$$3H_4SiO_4 - 4H_2O \rightarrow H_4Si_3O_8 \quad \text{Trisilicic acid.}$$

Di- and trisilicates are those derived from acids containing two and three units of silicon, respectively, in the formula.

The composition of minerals is often exceedingly complex. This is due to the fact that amongst them mixed salts (p. 359) are exceedingly common, in which the hydrogen of the imaginary acid is displaced by two or more metals in such a way that the total quantity of the metals is equivalent to the hydrogen. The following list presents in tabular form some typical or common minerals arranged according to the above mentioned classification:

Orthosilicates (H_4SiO_4)	Zircon,	$ZrSiO_4$
	Garnet,	$Ca_3Fe_2^{III}(SiO_4)_3$
	Mica,	$KH_2Al_3(SiO_4)_3$
	Kaolin,	$H_2Al_2(SiO_4)_2,H_2O$
Metasilicates (H_2SiO_3)	Wollastonite,	$CaSiO_3$
	Beryl,	$Gl_3Al_2(SiO_3)_6$
	Enstatite,	$MgSiO_3$
	Hornblende and augite	
Disilicate ($H_6S_2O_7$)	Serpentine,	$Mg_3Si_2O_7$,
Trisilicate ($H_4Si_3O_8$)	Orthoclase (feldspar),	$KAlSi_3O_8$

It will be seen that the total valence of the metal units is equal to that of the acid radicals. Thus, in beryl there are six equivalents of glucinum (beryllium) and six of aluminium, taking the place of twelve units of hydrogen in $(H_2SiO_3)_6$.

Mica, which is obtained in large sheets from Farther India, is used in making lamp-chimneys and as an insulator in electrical apparatus. **Kaolin**, or **clay**, like mica, is an acid orthosilicate. It is formed in nature as the result of the action of water and carbonic acid upon minerals like feldspar. In such cases, those elements which can form carbonates, like potassium, magnesium, and calcium, are usually displaced from combination with the silicic acid. Aluminium, however, is too feeble a base to form a carbonate, and is thus left in combination as silicate. A clay containing lime is called a **marl**, and one containing sand, a **loam**.

Some of these minerals frequently occur mixed together as regular components of certain igneous rocks. Thus, **granite** is a more or less coarse mixture of quartz, mica, and feldspar. Frequently the oblong, flesh-colored or white crystals of the last are large and very conspicuous. In **basalt** and **porphyry** the components are usually more intimately mixed and less easily visible to the eye. **Lava** is the name for any rock recently ejected from a volcano. **Pumice-stone** is the name given to the parts of the lava which are porous, having acquired this texture from the expansion of bubbles of gas consequent upon release of pressure. **Sandstone** is composed of sand cemented together by clay or by calcium carbonate, and colored brown or yellow by ferric oxide.

Since many silicates are not affected by acids, or at least are affected with extreme slowness, special means have to be taken to get the constituents of such minerals into soluble form for the purpose of analysis.

Two methods are in use. Sometimes the finely powdered mineral is heated in a platinum dish with hydrofluoric acid until all the silicon has passed off in the form of the tetrafluoride. Since the use of the fluorides would lead to difficulties in the course of the analysis, the resulting mixture of fluorides of the metals is next heated strongly with concentrated sulphuric acid, and the mixture of sulphates thus produced is treated according to the usual routine. In other cases the finely powdered mineral is fused at a white heat with a mixture of potassium and sodium carbonates. In this way carbonates of the metals are formed, along with potassium and sodium silicate. Treatment with water dissolves the latter, and leaves the carbonates to be handled in the usual way.

Boron.

As regards **chemical relations**, boron, being a uniformly trivalent element, is a member of the aluminium family. Yet it is a pronounced non-metal, and its oxide and hydroxide are almost wholly acidic; aluminium is a metal, and with its oxide and hydroxide basic properties predominate. Boron and its compounds really resemble carbon and silicon and their compounds in all chemical properties except the property of valence.

Occurrence. — Like silicon, boron is found in oxygen compounds, namely, in boric acid (*q.v.*) and its salts. Of the latter, sodium tetraborate $Na_2B_4O_7$, or borax, came first from India under the name of tincal. It constitutes a large deposit in Borax Lake in California. Colemanite, $Ca_2B_6O_{11}, 5H_2O$, from California, and other complex borates, furnish a large part of the commercial supply of compounds of boron.

Preparation. — When boric oxide is heated with powdered magnesium ($B_2O_3 + 3Mg \rightarrow 3MgO + 2B$), amorphous boron can be separated with some difficulty from the borides of magnesium in the resulting mixture. When excess of powdered aluminium is used, hard crystals of boron, containing aluminium, are found in the solidified metal. They may be separated by interaction of the metal with dilute hydrochloric acid.

Properties. — Amorphous boron is a black powder. It unites with the same elements as does silicon (p. 519), but with somewhat greater activity. Like carbon (p. 379), it is also oxidized by hot, con-

centrated sulphuric or nitric acid, the product being boric acid. The crystalline variety is less rapidly attacked in each case. Both kinds interact with fused potassium hydroxide, giving a borate:

$$2B + 6KOH \rightarrow 2K_3BO_3 + 3H_2$$

Hydrides and Halides of Boron. — When magnesium boride Mg_3B_2 is treated with hydrochloric acid, a gas containing much hydrogen, and possibly several hydrides of boron, is given off. By cooling the mixture with liquid air, Ramsay obtained a white solid which, when it resumed the gaseous condition, appeared to be B_3H_3.

By combined action of carbon and chlorine on boric oxide, using the principle employed in preparing silicon tetrachloride (p. 520), the **trichloride of boron** may be made. It is likewise formed by direct union of the free elements. It is also made easily by heating boric acid and phosphorus pentachloride, the action being an example of the behavior of the latter towards hydroxyl compounds (*cf.* p. 463):

$$B(OH)_3 + 3PCl_5 \rightarrow BCl_3 + 3POCl_3 + 3HCl.$$

The products are separated by fractional distillation. Boron trichloride is a liquid which boils at 18°, fumes strongly in moist air, and is completely hydrolyzed by water.

Boron trifluoride BF_3 is made by the interaction of calcium fluoride and sulphuric acid with boron trioxide. The mode of preparation and the properties of the substance recall silicon tetrafluoride (p. 521). It interacts with water, like the latter, giving boric acid and hydrofluoboric acid:

$$4BF_3 + 3H_2O \rightarrow B(OH)_3 + 3HBF_4.$$

The boric acid, not being very soluble, is precipitated. **Hydrofluoboric acid** is known only in solution, although many of its salts are stable.

Boric Acid. — Boric acid (boracic acid) is somewhat volatile with steam (*cf.* p. 471), and is found in Tuscany in jets of water vapor (*soffioni*) which issue from the ground. Water, retained in small basins by brickwork, is placed over the openings, and from this water, after evaporation by the help of the steam of the soffioni themselves, boric acid is obtained in crystalline form. As boric acid is very feeble, and withal little soluble, it may also be made by interaction of sulphuric acid and concentrated borax solution:

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \leftrightarrows Na_2SO_4 + 4H_3BO_3\downarrow.$$

Boric acid crystallizes from water in thin white plates, which are soapy (like graphite and talc) to the touch. Its solubility in water is 4 parts in 100 at 19° and 34 in 100 at 100°. The solution scarcely affects litmus. It confers a green tint on the Bunsen flame. The effect is best seen by setting fire to the vapor of a boiling alcoholic solution of the acid. This behavior is used as a **test** for the acid. At 100° the acid slowly loses water, leaving **metaboric acid** HBO_2, and at 140° **tetraboric acid** is formed: $4HBO_2 - H_2O \rightarrow H_2B_4O_7$. Strong heating gives the oxide B_2O_3. When dissolved in water, these dehydrated compounds revert to boric acid. The solution of boric acid in water is used as an antiseptic in medicine, and as a preservative for milk and other foods.

Borates. — Borates derived from orthoboric acid are practically unknown. The most familiar salt is **borax** or **sodium tetraborate.** The decahydrate $Na_2B_4O_7, 10H_2O$, which crystallizes from water at 27° in large, transparent prisms, and the pentahydrate which crystallizes at 56°,* are both marketed. They are made by crystallization of native borax. In Germany, borax is prepared from boracite, found at Stassfurt, by decomposing a solution of the mineral with hydrochloric acid:

$$MgCl_2, 2Mg_3B_8O_{15} + 12HCl + 18H_2O \rightarrow 7MgCl_2 + 16B(OH)_3.$$

The boric acid is redissolved in boiling water, and sodium carbonate is added:

$$4B(OH)_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + 6H_2O + CO_2.$$

In California it is made from colemanite by interaction with sodium carbonate.

Since boric acid is a feeble acid, borax is extensively hydrolyzed by water, and the solution has a marked alkaline reaction.

When heated with oxides of metals, sodium tetraborate behaves like sodium metaphosphate (*cf.* p. 468), and is used in the form of beads in analysis. If its formula be written $2NaBO_2, B_2O_3$, it will be seen that a considerable excess of the acid anhydride is contained in it, and that, therefore, a mixed metaborate may be formed by union with some basic oxide. Thus, with a trace of cupric oxide, the bead is tinged with green, from the presence of a compound like $2NaBO_2, Cu(BO_2)_2$. Cobalt compounds give a deep-blue color to the bead. For the same reason, borax is used in hard soldering. The hard solder

* For explanation of the relation of temperature of crystallization to degree of hydration, see under Manganous sulphate.

(brass) is placed, with a little borax, upon the joint between the objects of copper or brass which are to be soldered. At the temperature produced by the blast-lamp the borax dissolves the superficial coating of oxides, and the molten solder is able to "wet" the clean surfaces. A substance used thus, to bring infusible bodies into a fusible form of combination, is called a **flux**.

Boron Trioxide. — The oxide, as made by heating boric acid, is a glassy white solid. It is obtained also by burning boron in oxygen. Being almost perfectly involatile, it is able, when heated with salts, to displace other acid anhydrides which can be vaporized:

$$K_2SO_4 + B_2O_3 \rightleftarrows 2KBO_2 + SO_3\uparrow.$$

It has a slight tendency to act as a basic oxide. With fuming sulphuric acid it gives a boryl pyrosulphate BO,HS_2O_7 which is decomposed by water, and with phosphoric acid a phosphate BPO_4 which is stable.

Nitride and Carbide. — One of the difficulties in making free boron is due to its very great affinity for nitrogen, with which, when heated in the air, it unites to form a **nitride** BN. This compound is more easily made by heating borax with ammonium chloride:

$$Na_2B_4O_7 + 4NH_4Cl \rightarrow 4BN + 2NaCl + 7H_2O + 2HCl.$$

The nitride is a white solid which is easily decomposed when heated in a current of steam (*cf.* p. 417):

$$BN + 3H_2O \rightarrow B(OH)_3 + NH_3.$$

A **carbide of boron** B_6C is made by heating the free substances in the electric furnace. It is harder than carborundum, and stands next to the diamond in respect to hardness.

Exercises. — 1. Why is the fact that carborundum is not affected by water or acids worthy of mention?

2. Compare and contrast the elements carbon and silicon, and their corresponding compounds.

3. Why are there no colloidal solutions of iron and zinc (p. 524)?

4. What would be the interaction between aqueous solutions of an ammonium salt and of sodium orthosilicate?

CHAPTER XXXII

THE BASE-FORMING ELEMENTS

THERE are two ways in which the chemistry of a given set of elements may be described. We may take up the elements in succession, and discuss under each its physical and chemical properties, and the manufacture and behavior of a certain number of its compounds, such as the oxide, hydroxide, nitrate, and sulphate. Or we may arrange our major classification according to the properties and the forms of combination, and detail the facts about the same set of elements under each. Both methods have such advantages that neither can be sacrificed entirely. We shall, therefore, adopt the former plan for our division into chapters, following the usage already employed for the non-metals. In the present chapter a preliminary view of the chemistry of the metals will be given according to the second method.

Physical Properties of the Metals. — A knowledge of the physical properties of the metals is, to the chemist, of the greatest importance in connection with their manufacture and treatment. The following brief statement in regard to some of these properties is illustrative rather than exhaustive. It should be noticed that the properties of a metal vary according as the specimen has been prepared by rolling, casting, or some other process. Numerical values, therefore, when given, are only approximate.

Metals show what is commonly called a **metallic luster**, but, as a rule, they do so only when in compact form. Magnesium and aluminium exhibit it when powdered, but most of the metals when in this condition are black. In compact masses the metals are usually silvery white in color. Gold and copper, which are yellow and red respectively, are the conspicuous exceptions.

The metals can all be obtained in **crystallized form**, when a fused mass is allowed to cool slowly and the unsolidified portion is poured off. In almost all cases the crystals belong to the regular system. With the metals most nearly allied to the non-metals, however, they do not. Thus, the crystals of antimony and bismuth belong to the hexagonal system, and those of tin to the square prismatic.

The metals vary in **specific gravity** from lithium, which is little more than half as heavy as water (sp. gr. 0.59), to osmium, whose specific gravity is 22.5. Those which have a specific gravity less than 5, namely, potassium, sodium, calcium, magnesium, aluminium, and barium, are called the light metals, and the others the heavy metals.

Most metals are **malleable**, and can be beaten into thin sheets without loss of continuity. Those which are allied to the non-metals, however, such as arsenic, antimony, and bismuth, are brittle, and can be reduced to powder in a mortar. Zinc becomes malleable only when heated to 150°. The order of the elements in respect to this property, beginning with the most malleable, is: Au, Ag, Cu, Sn, Pt, Pb, Zn, Fe, Ni.

The **tenacity** of the metals places them in an order different from the above. It is measured by the number of kilograms which a piece of the metal 1 sq. mm. in section can sustain without breaking. The values are as follows: Fe 62, Cu 42, Pt 34, Ag 29, Au 27, Al 20, Zn 5, Pb 2.

The **hardness** is measured by the ease with which the material may be disintegrated by a sharp, hard instrument. Potassium is as soft as wax, while chromium is hard enough to cut glass.

The **temperature** at which the metal **fuses** has an important bearing on its manufacture. Most of the following melting-points are only approximate:

Mercury . .	−40°	Zinc . . .	420°	Cast iron . .	1150°
Potassium .	62°	Antimony .	437°	Nickel . . .	1500°
Sodium . .	96°	Aluminium .	700° (?)	Platinum . .	1780°
Tin . . .	230°	Magnesium .	750°	Iron (pure) .	1800°
Bismuth . .	264°	Silver . .	954°	Manganese .	1900°
Cadmium .	320°	Copper . .	1057°	Chromium .	2000°
Lead . . .	326°	Gold . . .	1075°	Iridium . .	2200°

It will be seen that mercury is a liquid, that potassium and sodium melt below the boiling-point of water, and that the metals down to the foot of the second column can be melted easily with the Bunsen flame. The metals osmium, molybdenum, uranium, tungsten, and vanadium have melting-points above the melting-point of platinum.

The methods of manufacture and the treatment of metals are much influenced also by their **volatility**. The following are easily distilled: Mercury, b.-p. 357°; potassium and sodium, b.-p. about 700°; cadmium, b.-p. 770°; zinc, b.-p. 950°. Even the most involatile metals can be converted into vapor in the electric arc.

In many cases molten metals dissolve in one another freely. The mixtures are called **alloys**, and in some cases have the properties of solid solutions. Sometimes, as in the case of lead and tin, mixtures can be formed in all proportions. On the other hand, the solubility may be limited, as in the case of zinc and lead, where only 1.6 parts of the former dissolve in 100 parts of the latter. The colors of alloys are not the average of those of the constituents. Thus, a mixture containing copper with 30 per cent of tin is perfectly white. A similar mixture with 30 per cent of zinc is pale yellow. The nickel alloy used in coining contains 75 per cent of copper and 25 per cent of nickel, yet it shows none of the color of the former. Thirty per cent of gold may be added to silver without conferring any yellow tint upon it.

Some of the properties of alloys are classifiable by the ordinary laws of solution. Thus, a foreign body lowers the vapor tension of a solvent (p. 161), and so the presence of a foreign metal diminishes the ease with which particles can be torn from the surface by any means whatever. That is to say, it increases the hardness. A foreign metal also lowers the melting-point (p. 163). In many cases the metal becomes less active when alloyed. Thus, a mixture of gold and silver containing twenty-five per cent of the latter does not interact visibly with nitric acid. It is necessary to bring the amount of silver up to 75 per cent at least ("quartation") in order that the silver may be freely attacked by the warm acid. The gold remains in any case untouched. The malleability and the conductivity for heat and electricity are diminished by addition of a foreign metal. Copper, whose commercial applications depend largely on the first and third of these properties, is much affected in respect to them by the presence of even small traces of impurities.

Alloys in which mercury forms one of the components are known as **amalgams** (Gk. μάλαγμα, a soft mass), and are formed with especial ease by the lighter metals. Of the common metals, iron is the least miscible with mercury.

The good **conductivity** of metals for **electricity** distinguishes them with some degree of sharpness from the non-metals. They show considerable variation amongst themselves, silver conducting sixty times as well as mercury. The conductivity increases as the temperature is lowered, and this fact is taken advantage of in the measurement of the temperature of liquefied gases. The platinum resistance thermometer consists chiefly of a wire of platinum. The resistance of this metal diminishes so rapidly, with decreasing temperature, that measurement

of its resistance can be used for the accurate determination of the temperature. In the following table the conductivities of the metals are expressed in terms of the number of meters of wire 1 sq. mm. in section which, at 15°, offer a resistance of one ohm:

Silver, cast	62.89	Nickel, cast	7.59
Copper, commercial	57.40	Iron, drawn	7.55
Gold, cast	46.30	Platinum	5.7–8.4
Aluminium, commercial	31.52	Steel	5.43
Zinc, rolled	16.95	Lead	4.56
Brass	14.17	Mercury	1.049

The resistance at 0° of a column of mercury 1 sq. mm. in section and 1.063 meters long is called the ohm, and is employed in expressing the conductivities of solutions (p. 328). To compare the above figures with those given for solutions, however, it must be recalled that, in the measurement of the conductivities of the latter, a column only 1 cm. in length and of 1 sq. cm. area was employed, so that the figures representing the conductivities of solutions are on a scale approximately ten thousand times as great as those presented in the above table. Thus, normal hydrochloric acid (p. 328) has a conductivity on the above scale of 0.0301, or less than a thirtieth of that of mercury

General Chemical Relations of the Metallic Elements.— Since most of the compounds of the metals are ionogens, their solutions, except when the metal is a part of a compound ion or of a complex ion (see below), all contain the metal in the ionic state, and the resulting substances, such as kalion and cuprion, have constant properties, irrespective of the nature of the negative ion with which they may be mixed. The properties of the ions, simple and compound, are much used in making tests in analytical chemistry. On the other hand, the chemical properties of the oxides and of the salts in the *dry state* are of importance in connection with metallurgy.

There are **six chemical properties which are more or less generally characteristic of the metallic elements.** The first two of them have already been discussed somewhat fully.

1. The metals are able by themselves to form *positive* radicals of salts, and, therefore, to exist alone as positive ions (pp. 337, 404).

2. The oxides and hydroxides of the metals are basic (pp. 119, 404).

3. The halogen compounds of the *typical* metals are little, if at all, hydrolyzed by water (see next section).

These three properties are characteristic of *all* metals, and form the basis of the distinction between metals and non-metals. The remaining three apply to many metals, but no one of them applies to all.

4. An oxide or hydroxide which is basic may also be acidic, as, for example, zinc hydroxide (p. 405). Even when this is not the case, some other oxide of the metal may be acidic exclusively, as is manganese heptoxide (p. 405). In consequence of either of these facts, a metal may form *part* of the negative radical of a simple salt, and therefore be found in a negative ion, as, ZnO_2'' or MnO_4'.

5. Some salts of certain metals combine with those of others to give complex salts (p. 363 and next section but one). Of this sort are the complex cyanides, such as $K.Ag(CN)_2$ and $K_4.Fe(CN)_6$. A metal thus forms part of the negative radical of a salt of a complex acid, and therefore is found in an anion like $Ag(CN)_2'$ or $PtCl_6''$.

6. Some metals also form parts of complex cations which are contained in solutions of molecular compounds (p. 443), chiefly those of salts with ammonia. Thus, when $AgCl, 3NH_3$ is dissolved in water, or when ammonium hydroxide is added to a solution of a salt of silver, the positive ion is found to be $Ag(NH_3)_2^{\cdot}$ (see under Copper). (For a detailed illustration of the application of these six criteria, see discussion of the chemical relations in the nitrogen family, Chap. xli.)

Aside from these points, many features in the behavior of metals and their compounds are summed up in the electromotive series (p. 362). The reader should re-read all the parts referred to above before proceeding farther. He should also reëxamine the various kinds of chemical changes discussed on p. 187 and particularly the varieties of ionic chemical change on p. 360.

Hydrolysis of Halogen Compounds, Used to Distinguish Metals from Non-Metals. — We have seen that the halogen compounds of phosphorus (p. 463), of sulphur (p. 398), of silicon (p. 521), and of other non-metals, are completely hydrolyzed by water, giving the hydrogen halide, and an acid which contains the hydroxyl of the water:

$$PCl_3 + 3HOH \rightarrow 3HCl + P(OH)_3.$$

Now, those elements whose halogen compounds are *not* hydrolyzed by water, or, at all events, are only partly hydrolyzed, are the ones classed as metals. Thus, sodium chloride is not decomposed appreciably by

water, and cupric chloride, like cupric sulphate (p. 344), is but slightly hydrolyzed, and its solution has a faint acid reaction:

$$CuCl_2 + 2H_2O \leftrightarrows 2HCl + Cu(OH)_2.$$

In a few cases, as with the chlorides of antimony (*q.v.*) and of bismuth (*q.v.*), a considerable proportion, but not all, of the halogen is removed from each molecule:

$$SbCl_3 + H_2O \rightleftarrows 2HCl + SbOCl\downarrow.$$

The resulting mixture is strongly acid, and the product (antimony oxychloride) is a definite compound, of the nature of a mixed salt (p. 359), known as a basic salt. The difference is that, with the halides of the *metals*, the action of water is notably *reversible*, while with halides of the *non-metals* it is not so.

Hydrolysis of the halides of the metals is increased by rise in temperature and by dilution of the solution (addition of more water), and also gains headway when one of the products of hydrolysis is thrown down as a precipitate. The last two influences are the ones which normally permit a reversible action to approach completion (p. 259).

The halogen compounds are chosen as the basis of this criterion because the halogen acids are active and would reverse the hydrolysis completely, and leave no acid reaction, if the result depended upon them alone. It is the lack of activity in the base, and the tendency of its *molecules* to be formed from the metal ions of the salt and the OH′ of the water (p. 314), that determine the slight hydrolysis, when it occurs. Thus, this criterion is simply another means of recognizing whether or not the hydroxide of the element is a strong (much ionized) base, and its application gives, therefore, the same result in each case as does the employment of the second of the chemical characteristics of metallic elements (see above).

Other, non-halide salts of the metals, even of the most active, may be extensively hydrolyzed by water. Thus, sodium sulphide is decomposed by it (p. 375) to the extent of one-half. But here the solution is *alkaline* in reaction:

$$Na_2S + H_2O \rightarrow NaSH + NaOH,$$

owing to the small ionization of the SH′ ion, and the result is due to the feebleness of the acid (H_2S). Indeed, the great activity of the base is demonstrated by the final reaction of the solution, and the

metallic nature of sodium is therefore not impugned by the existence of hydrolysis *per se* in such a salt as this, but is rather confirmed.

To sum up: An alkaline reaction shows that we have a solution of a salt of an active metal with a weak acid; an acid reaction that we have a salt of an inactive metal, which may even verge on the non-metallic, with an active acid. Salts of two active components give neutral solutions. Thus, as a particular case, the halogen compounds of the typical metals are not perceptibly hydrolyzed by water, and the hydrolysis of the halide of a less pronounced metal takes place with acid reaction, and is easily reversible by excess of either product. A salt of an acid and base both of which are weak is hydrolyzed, often completely. Aluminium carbonate and ammonium silicate are examples of salts which, for this reason, are completely hydrolyzed. The resulting mixture may have an acid or a basic reaction, if the acid or the base is sufficiently soluble and sufficiently active. Thus, ammonium sulphide solution is alkaline.

Salts of Complex Acids. — These salts are of many classes, and arise by direct union of two salts. Thus we have cyanides like $K.Ag(CN)_2$ (potassium argenticyanide), $K.Cu(CN)_2$ (potassium cuprocyanide), and $K_4.Fe(CN)_6$ (potassium ferrocyanide):

$$K.CN + AgCN \uparrow \rightarrow K.Ag(CN)_2.$$

The complex sulphur compounds of arsenic, antimony, and tin (*q.v.*), such as sodium sulphostannate $Na_2.SnS_3$, are made in the same way:

$$Na_2.S + SnS_2 \uparrow \rightleftarrows Na_2.SnS_3.$$

Many double halides are of a like nature, as $K_2.PtCl_6$ (potassium chloroplatinate), $H_2.PtCl_6$ (chloroplatinic acid), and $Na.AuCl_4$ (sodium chloraurate). In every case the metal of one of the original salts is contained in the negative radical (the anion). Hydrofluosilicic acid (p. 521) is a compound analogous to those of the last group, excepting that SiF_4, from which it is formed, is not a salt, and silicon is not a metal.

The characteristic of these compounds is that, when they are ionized, the less positive metal is contained in a complex anion like $Ag(CN)_2'$, SnS_3'', $PtCl_6''$. In fact, they behave, in most respects, like ordinary single salts. Thus, they undergo double decomposition in the normal manner, the complex ion acting as a whole. For example, a soluble ferrocyanide with a zinc salt gives zinc ferrocyanide:

$$K_4.Fe(CN)_6 + 2Zn.SO_4 \rightleftarrows Zn_2Fe(CN)_6 \downarrow + 2K_2.SO_4.$$

This behavior distinguishes salts of complex acids from double salts (p. 360). In typical cases the latter resemble the former, indeed, only in their mode of preparation (by union of two simple salts), and in solution are resolved once more into the component salts and their separate ions. The distinction must be regarded, however, only as a means of rough classification for practical purposes. In reality, all complex ions give at least a trace of the simpler ions, and many are decomposed to a noticeable extent. At the other extreme, the double salts form complex ions in appreciable amounts in concentrated solutions.

In harmony with the above characteristic, salts of complex acids, like potassium ferrocyanide, when treated with acids, like sulphuric acid, undergo double decomposition, and give the free complex acid (here ferrocyanic acid):

$$K_4.Fe(CN)_6 + 2H_2.SO_4 \rightleftarrows H_4Fe(CN)_6 \downarrow + 2K_2.SO_4.$$

But in many cases the acids are unstable, those of the cyanides, for example, giving up hydrocyanic acid and those of the complex sulphur compounds, hydrogen sulphide:

$$H_2.SnS_3 \leftrightarrows H_2S \uparrow + SnS_2 \downarrow.$$

The complex halogen acids, however, like $H_2.PtCl_6$ and $H.AuCl_4$, are stable, and are fairly active as acids.

The similarity of these compounds to oxygen acids, and their salts, may be seen if we imagine them to be cases in which cyanogen, sulphur, chlorine, and other radicals have taken the place of oxygen in the anion. Thus, $[(CN)_2]^{II}$, $[Cl_2]^{II}$, and S^{II} are equivalent to O^{II}. Many of the corresponding oxygen compounds are actually known, as sodium stannate $Na_2.SnO_3$ and sodium aurate $Na.AuO_2$, corresponding respectively to $Na_2.SnS_3$ and $Na.AuCl_4$.

The behavior of complex ions is discussed further under Copper.

Classification of the Metallic Elements by their Chemical Relations. — In treating of the metallic elements and their compounds we shall use the groupings provided by the periodic system (p. 411). A division into eleven sets, which are described briefly, and in general terms below, will be sufficient for the purpose of this book:

1. **Metals of the Alkalies.** — Lithium, sodium, potassium, rubidium, caesium, and the radical ammonium NH_4. These metals are univalent, and their oxides and hydroxides have strongly basic properties. Their salts with active acids are not hydrolyzed in solution.

2. **Metals of the Alkaline Earths.** — Calcium, strontium, barium,

and, possibly, radium. These metals are bivalent in all their compounds. Their oxides and hydroxides are strongly basic, but the latter are not so soluble in water as are the hydroxides of the former family. The salts with active acids are not hydrolyzed.

3. **Copper, Silver, and Gold.** — These metals occupy the right-hand side of the second column of the table (p. 411). Their alliance with the alkali metals, their neighbors, is rather remote. Each of them, however, gives compounds in which it is univalent, although, in their commoner compounds, copper and gold are bivalent and trivalent, respectively. The oxides and hydroxides of copper and gold have rather weak basic properties; those of silver are much more active.

4. **Beryllium, Magnesium, Zinc, Cadmium, and Mercury.** — These metals, occupying the right-hand side of the third column, are bivalent, although mercury forms a series of compounds in which it is univalent as well. The oxides and hydroxides are feebly basic, those of magnesium being the most basic.

5. **Aluminium** and the other metals on both sides of the fourth column. — The metals of these groups are trivalent, and the oxides and hydroxides are feebly basic in character. The hydroxide of aluminium has also a feebly acidic tendency.

6. **Germanium, Tin, and Lead, and the Titanium Family.** — In accordance with their position in the periodic table these metals are all quadrivalent. At the same time they act also as bivalent elements, the compounds of this class in the case of lead being the more familiar. The oxides and hydroxides are feebly basic, and are able also to play the rôle of acidic oxides towards strong bases.

7. **Arsenic, Antimony, and Bismuth,** and the metals of the **Vanadium Group.** — These elements, like nitrogen and phosphorus, form two sets of compounds in which they are trivalent and quinquivalent, respectively. The acidic tendency of the oxides and hydroxides, which in the last column was noticeable, is here much more pronounced. Both oxides of arsenic are almost wholly acidic in behavior, and the pentoxides of the other elements are likewise acid anhydrides exclusively. The trioxides are basic in a feeble way, and their salts are much hydrolyzed by water.

8. **Chromium, Molybdenum, Tungsten, and Uranium.** — These elements, occupying the left-hand side of the seventh column, exhibit a considerable variety of valence. The maximum, however, is six in each case. The oxides of the form CrO and Cr_2O_3, in which the elements are bivalent and trivalent, are base-forming. Those of the form CrO_3, in

which the elements are sexivalent, resemble sulphur trioxide and are acid anhydrides.

9. **Manganese.** — This element, the only one in the eighth column which has not yet been treated, gives several series of compounds in which its valence varies from 2 to 7. Compounds derived from the basic oxide MnO are the salts in which manganese is most distinctly a metallic element. The highest oxide, Mn_2O_7, is an acid anhydride.

10. **Iron, Nickel, and Cobalt.** — These elements give oxides which are feebly basic. Iron gives two extensive series of compounds in which it is bivalent and trivalent, respectively. Those of the former set resemble the bivalent salts of manganese and zinc. Those of the latter resemble the salts of aluminium. Cobalt and nickel in most of their compounds are bivalent elements, and the behavior recalls that of the compounds of bivalent manganese and zinc.

11. **Palladium and Platinum Families.** — The metals of these families have little chemical activity, and their compounds are easily decomposed by heating. Along with gold, silver, and mercury, which have similar characteristics, they are sometimes grouped together under the name of the *noble metals*.

Occurrence of the Metals in Nature.—The minerals from which metals are extracted are known as *ores*. They present a comparatively small number of different kinds of compounds. Most of the metals are found in more than one of these forms, so that in the following statement the same metal frequently occurs more than once.

When the metal occurs free in nature it is said to be **native**. Thus we have native gold, silver, metals of the platinum group, copper, mercury, bismuth, antimony, and arsenic (*cf.* p. 362).

The metals whose **oxides** are important minerals are iron, manganese, tin, zinc, copper, and aluminium. The metals are obtained commercially from the oxides in each of these cases.

The metals whose **sulphides** are used as ores are nickel, cobalt, antimony, lead, cadmium, zinc, and copper.

From the **carbonates** we obtain iron, lead, zinc, and copper. Several other metals, such as manganese, magnesium, barium, strontium, and calcium occur in larger or smaller quantities in the same form of combination.

The metals which occur as **sulphates** are those whose sulphates are not freely soluble, namely, lead, barium, strontium, and calcium.

Compounds of metals with the **halogens** are not so numerous. Silver chloride furnishes a limited amount of silver. Sodium and potassium chlorides are found in the salt-beds, and cryolite $3NaF, AlF_3$ is used in the manufacture of aluminium.

The natural **silicates** are very numerous, but are seldom used for the preparation of the metals. Many of them are employed for other commercial purposes, kaolin (p. 525) being a conspicuous example of this class.

Methods of Extraction from the Ores. — The art of extracting metals from their ores is called **metallurgy**. Where the metal is **native**, the process is simple, since melting away from the matrix (p. 367) is all that is required. Frequently a flux (p. 529) is added, which combines with the matrix, giving a fusible **slag**. Since the slag is a melted salt, usually a silicate, and does not mix at all with the molten metal, separation of the products is easily effected. When the ore is a compound, the metal has to be liberated by furnishing a material capable of combining with the other constituent. The details of the process depend on various circumstances. Thus the volatile metals, like zinc and mercury, are driven off in the form of vapor, and secured by condensation. The involatile metals, like copper and iron, run to the bottom of the furnace and are tapped off.

Where the ore is an **oxide** it is usually reduced by heating with carbon in some form. This holds for the oxides of iron and copper, for example. Some oxides are not reducible by carbon in an ordinary furnace. Such are the oxides of calcium, strontium, barium, magnesium, aluminium, and the members of the chromium group. At the temperature of the electric furnace even these may be reduced, but the carbides are formed under such circumstances, and the metals are more easily obtained otherwise. Recently, heating the pulverized oxide with finely powdered aluminium has come into use, particularly for operations on a small scale. Iron oxide is easily reduced by this means, and even the metals manganese and chromium may be liberated from their oxides quite readily by this action. This procedure has received the name *aluminothermy* (*q.v.*) on account of the great amounts of heat liberated. In the laboratory the oxides of the less active metals are frequently reduced in a stream of hydrogen (*cf.* p. 362).

When the ore is a **carbonate**, it is first heated strongly to drive out the carbon dioxide (*cf.* p. 480): $FeCO_3 \rightleftarrows FeO + CO_2 \uparrow$, and then the oxide is treated according to one of the above methods. When the

ore is a **sulphide**, it has to be roasted (*cf.* p. 378) in order to remove the sulphur, and the resulting oxide is then treated as described above.

Chlorides and **fluorides** of the metals can be decomposed by heating with metallic sodium (*cf.* p. 518). This method was formerly employed in the making of magnesium and aluminium.

The metals which are not readily secured in any of the above ways, can be obtained easily by **electrolysis** of the fused chloride or of some other simple compound. Aluminium is now manufactured entirely by the electrolysis of a solution of aluminium oxide in molten cryolite.

Compounds of the Metals: Oxides and Hydroxides. — The **oxides** may be made by direct burning of the metal, by heating the nitrates (*cf.* p. 444), the carbonates (*cf.* p. 480), or the hydroxides: $Ca(OH)_2 \rightleftarrows CaO + H_2O \uparrow$. They are practically insoluble in water, although those of the metals of the alkalies and of the metals of the alkaline earths interact with water rapidly to give the hydroxides. They are usually stable. Those of gold, platinum, mercury, and silver decompose when heated, yet with increasing difficulty in this order. The metals, like the non-metals, frequently give several different oxides. Those of the univalent metals, having the form K_2O, if we leave cuprous oxide and aurous oxide out of account, have the most strongly basic qualities. Those of the bivalent metals of the form MgO, when this is the only oxide which they furnish, are base-forming. Those of the trivalent metals of the form Al_2O_3 are the least basic of the basic oxides. The oxides of the forms SnO_2, Sb_2O_5, CrO_3, and Mn_2O_7, in which the metals have valences from 4 to 7, are mainly acid-forming oxides, although the same elements usually have other lower oxides, which are basic.

The **hydroxides** are formed, in the cases of the metals of the alkalies and alkaline earths by direct union of water with the oxides. They are produced also by double decomposition when a soluble hydroxide acts upon a salt (*cf.* p. 350). All hydroxides, except those of the alkali metals, lose the elements of water when heated, and the oxide remains. In some cases the loss takes place by stages, just as was the case with orthophosphoric acid (p. 465). Thus lead hydroxide $Pb(OH)_2$ (*q.v.*) first gives the hydroxide $Pb_2O(OH)_2$, then $Pb_3O_2(OH)_2$, and then the oxide PbO. With the exception of those of the metals of the alkalies and alkaline earths, all the hydroxides are little soluble in water. The hydroxides of mercury and silver, if they are formed at all, are evidently unstable, for, when either material is dried, it is found to contain nothing but the corresponding oxide.

Compounds of the Metals: Salts. — It may be said, in general, that each metal may form a salt by combination with each one of the acid radicals. In the succeeding chapters we shall describe only those salts which are manufactured commercially, or are of special interest for some other reason. The various salts will be described under each metal. Here, however, a few remarks may be made about the characteristics of the more common groups of salts. The salts are classified according to the acid radicals which they contain.

The **chlorides** may be made by the direct union of chlorine with the metal (*cf.* p. 74), or by the combined action of carbon and chlorine upon the oxide (*cf.* p. 520). The latter method is used in making chromium chloride. The general methods for making any salt (p. 186), such as the interaction of a metal with an acid, or of the oxide, hydroxide, or another salt with an acid, or the double decomposition of two salts, may be used also for making chlorides. The chlorides are for the most part soluble in water. Silver chloride, mercurous chloride, and cuprous chloride are almost insoluble, however, and lead chloride is not very soluble. Most of the chlorides of metals dissolve without decomposition, but hydrolysis is conspicuous in the case of the chlorides of the trivalent metals, such as aluminium chloride and ferric chloride (*cf.* p. 344). The chlorides of some of the bivalent metals are hydrolyzed also, but, as a rule, only when they are heated with water. This is the case with the chlorides of magnesium, calcium, and zinc. Most of the chlorides are stable when heated, but those of the noble metals, particularly gold and platinum, are decomposed, and chlorine escapes. The chlorides are usually the most volatile of the salts of a given metal, and so are preferred for the production of the spectrum (*q.v.*) of the metal, and for fixing the atomic weight of the metal by use of the vapor density. Some of the metals form two or more different chlorides. For example, indium gives $InCl$, $InCl_2$, and $InCl_3$.

The **sulphides** are formed by the direct union of the metal with sulphur, or by the action of hydrogen sulphide or of some soluble sulphide upon a solution of a salt (*cf.* p. 375). In one or two cases they are made by the reduction of the sulphate with carbon. The sulphides, except those of the alkali metals, are but little soluble in water. The sulphides of aluminium and chromium are hydrolyzed completely by water, giving the hydroxides, and those of the metals of the alkaline earths are partially hydrolyzed (*cf.* p. 376).

Some of the metals, when they are in the molten form, simply dissolve carbon, and, when they are cooled once more, deposit it in the

form of graphite. This is true particularly of platinum and iron. The **carbides** are usually formed in the electric furnace by interaction of an oxide with carbon (*cf.* p. 478). Some of them are decomposed by contact with water, after the manner of calcium carbide, giving a hydroxide and a hydrocarbon. Of this class are lithium carbide Li_2C_2, barium and strontium carbides BaC_2 and SrC_2, aluminium carbide Al_4C_3, manganese carbide MnC, and the carbides of potassium and glucinum. Others, such as those of molybdenum CMo_2 and chromium Cr_3C_2, are not affected by water.

The **nitrates** may be made by any of the methods used for preparing salts. They are *all* at least fairly soluble in water.

The **sulphates** are made by the methods used for making salts, and in some cases by the oxidation of sulphides. They are all soluble in water, with the exception of those of lead, barium, and strontium. Calcium sulphate is meagerly soluble.

The **carbonates** are prepared by the methods used for making salts. They are all insoluble in water, with the exception of those of sodium and potassium. The hydroxides of aluminium and tin are so feebly basic that these metals do not form stable carbonates (*cf.* pp. 119, 523).

The **phosphates** and **silicates** are prepared by the methods used in making salts. The former are obtained also by special processes already described (p. 467). With the exception of the salts of sodium and potassium, all the salts of both these classes are insoluble.

Solubility of Bases and Salts. — The solubilities of a few salts at various temperatures have already been given (p. 157). The following table includes a much larger number of substances (142), and gives the solubility at 18°. Each square contains two numbers expressing the solubility of the compound whose cation stands at the head of the column and whose anion is indicated at the side. The solubility is that of the hydrate stable at 18°, where such exists. The **upper number** in each case gives the number of grams of the anhydrous salt held in solution by 100 c.c. of water. The **lower number** shows the number of moles in 1 l. of the saturated solution, and indicates therefore the concentration in terms of a molar solution as unity — the molar solubility. In the cases of the less soluble compounds the values are not exact, but they will serve to show roughly the relative solubilities when several substances are compared. The numbers for small solubilities have been abbreviated. Thus, $0.0_64 =$ 0.0000004.

Solubility of Bases and Salts in Water at 18°.

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95 3.9	35.86 5.42	77.79 13.3	$0.0_{3}16$ $0.0_{4}10$	0.3 0.013	37.24 1.7	51.09 3.0	73.19 5.4	55.81 5.1	203.9 9.2	1.49 0.05
Br	65.86 4.6	88.76 6.9	168.7 12.6	$0.0_{4}1$ $0.0_{6}6$	0.04 $0.0_{2}15$	103.6 2.9	96.52 3.4	143.3 5.2	103.1 4.6	478.2 9.8	0.598 0.02
I	137.5 6.0	177.9 8.1	161.5 8.5	$0.0_{6}3$ $0.0_{7}1$	0.006 $0.0_{3}17$	201.4 3.8	169.2 3.9	200 4.8	148.2 4.1	419 6.9	0.08 $0.0_{2}2$
F	92.56 12.4	4.44 1.06	0.27 0.11	195.4 13.5	72.05 3	0.16 $0.0_{2}92$	0.012 0.001	0 0016 $0.0_{3}2$	0.0076 $0.0_{2}14$	0.005 $0.0_{3}5$	0.07 0.003
NO_3	30.34 2.6	83.97 7.4	71.43 7.3	213.4 8.4	8.91 0.35	8.74 0.33	66.27 2.7	121.8 5.2	74.31 4.0	117.8 4.7	51.66 1.4
ClO_3	6.6 0.52	97.16 6.4	313.4 15.3	12.25 0.6	3.69 0.13	35.42 1.1	174.9 4.6	179.3 5.3	126.4 4.7	183.9 5.3	150.6 3.16
BrO_3	6.38 0.38	36.67 2.2	152.5 8.20	0.59 0.025	0.30 0.009	0.8 0.02	30.0 0.9	85.17 2.3	42.86 1.5	58.43 1.8	1.3 0.03
IO_3	7.62 0.35	8.33 0.4	80.43 3.84	0.004 $0.0_{3}14$	0.059 $0.0_{2}16$	0.05 0.001	0.25 $0.0_{2}57$	0.25 0.007	6.87 0.26	0.83 0.02	0.002 $0.0_{4}3$
OH	142.9 18	116.4 21.	12.04 5.0	0.01 0.001	40.04 1.76	3.7 0.22	0.77 0.063	0.17 0.02	0.001 $0.0_{3}2$	$0.0_{3}5$ $0.0_{4}5$	0.01 $0.0_{3}4$
SO_4	11.11 0.62	16.83 1.15	35.64 2.8	0.55 0.020	4.74 0.09	$0.0_{3}23$ $0.0_{4}10$	0.011 $0.0_{3}6$	0.20 0.015	35.43 2.8	53.12 3.1	0.0041 $0.0_{3}13$
CrO_4	63.1 2.7	61.21 3.30	111.6 6.5	0.0025 $0.0_{3}15$	0.006 $0.0_{3}1$	$0.0_{3}38$ $0.0_{4}15$	0.12 0.006	0.4 0.03	73.0 4.3	. . . . . .	$0.0_{4}2$ $0.0_{6}5$
C_2O_4	30.27 1.6	3.34 0.24	7.22 0.69	0.0035 $0.0_{3}2$	1.48 0.030	0.0086 $0.0_{3}38$	0.0046 $0.0_{3}26$	$0.0_{3}56$ $0.0_{4}43$	0.03 0.0027	$0.0_{3}6$ $0.0_{4}4$	$0.0_{3}15$ $0.0_{5}5$
CO_3	108.0 5.9	19.39 1.8	1.3 0.17	0.003 $0.0_{3}1$	4.95 0.10	0.0023 $0.0_{3}11$	0.0011 $0.0_{4}7$	0.0013 $0.0_{3}13$	0.1 0.01	0.004? $0.0_{3}3$?	$0.0_{3}1$ $0.0_{4}3$

The following are the solubilities (number of grams in 100 c.c. water) at 18° of two additional insoluble substances and of three acid salts.

Mercurous chloride, $0.0_{3}2$
(molar sol'ty, $0.0_{4}1$)
Mercuric iodide, $0.0_{4}4$
(molar sol'ty, $0.0_{5}1$)

Sodium bicarbonate	9.6
Potassium bicarbonate	26.1
Potassium bisulphate	50.0

It will be seen that some compounds, like zinc chloride and barium iodide, are exceedingly soluble; that others, like potassium chloride and barium chlorate, are of medium solubility; that still others, like calcium hydroxide and calcium sulphate, are sparingly soluble; and, finally, that some, like calcium oxalate (CaC_2O_4) and barium chromate, are almost insoluble. The reader should note the fact, however, that the differences in solubility even amongst the insoluble salts are as great as amongst the soluble ones.

Hydrated Forms of Salts Commonly Used. — In the table given below, the figures refer to the number of molecules of water in the hydrates which are deposited by aqueous solutions of the salts in the neighborhood of 18°. The letter *h* means that the compound is stable when *heated*, the letter *a* that it is not affected by the *air*, the letter *d* that the salt is *deliquescent*, and the letter *e* that the hydrate loses water spontaneously in an open vessel, *i.e.*, is *efflorescent.*

Composition of Hydrates of Salts.

	K	Na	Li	Ag	Ba	Sr	Ca	Mg	Zn	Cd	Cu	Pb
Cl	0*h*	0*h*	0*h*	0*h*	2*a*	6*e*	6*d*	6*d*	1½*d*	2½*e*	2*d*	0*h*
Br	0*h*	0*h*	0*h*	0*h*	2*a*	6*d*	6*d*	6*d*	2*d*	4*e*	4*e*	0*h*
I	0*h*	0*h*	0*h*	0*h*	2*d*	6*d*	0*d*	8*d*	0*d*	0*a*	. .	0*h*
NO_3	0*a*	0*a*	0*d*	0*a*	0*a*	4*e*	4*d*	6*d*	6*d*	4*d*	6*d*	0*a*
ClO_3	0*a*	0*a*	0*d*	0*a*	1*a*	5*d*	2*d*	6*d*	6*d*	2*d*	6*d*	1*a*
BrO_3	0*a*	0*a*	0*d*	0*a*	1*a*	1*a*	1*a*	6*e*	6*a*	2*a*	6*a*	1*a*
IO_3	0*a*	3*e*	0*d*	0*a*	1*a*	6*e*	6*e*	4*a*	2*a*	0*a*	1*a*	0*a*
$C_2H_3O_2$	0*d*	3*d*	2*d*	0*a*	1*a*	½*a*	2*d*	4*d*	3*a*	3*d*	1*a*	3*a*
SO_4	0*h*	10*e*	0*h*	0*a*	0*h*	0*h*	2*a*	7*e*	7*e*	2⅔*a*	5*a*	0*h*
CrO_4	0*h*	10*e*	2*a*	0*a*	0*h*	0*h*	1*a*	7*e*	. .	. .	. .	0*h*
C_2O_4	1*a*	0*a*	0*a*	0*a*	1*a*	0*a*	1*a*	2*a*	2*a*	3*a*	1*a*	0*a*
CO_3	1½*d*	10*e*	0*a*	0*e*	0*h*	0*h*	0*a*	3*e*	0*a*	0*a*	. .	0*a*

Isomorphism. — Substances which crystallize in one of the forms belonging to the regular system (p. 138) must necessarily have identical crystalline shapes. Thus, crystallized specimens of sodium chloride and of lead sulphide (galena) in their natural shapes are cubical. The forms found in other systems, however, are capable of assuming an infinite diversity of shapes. The relative lengthening or shortening in one direction, shown by the square prismatic and hexagonal forms (p. 138), for example, makes it possible for each separate substance to adopt proportions which are more or less different

from those of every other substance. Each substance, not belonging to the regular system, does, in fact, crystallize invariably in forms based upon its own fundamental proportions, and differs therefore in its angles from all other such substances in a way that is clearly recognizable by refined measurement.

Now it is found that substances which are chemically somewhat similar (see below) frequently crystallize in the same system and show proportions which are almost, although not quite, identical. Furthermore, such substances, when the approach to identity in angles is not accidental, can take part in the construction of one and the same crystal. A crystal of one such substance placed in a solution of the other will continue to grow, and in doing so will follow the pattern already set, and simply increase in dimensions by accretion of the new material. When a solution containing two such substances deposits crystals, the structures are, not some of them of one material and some of the other, but are all made up of *both* in a ratio determined by the relative amounts of the substances in the solution.* **Substances** related in these two ways, that is, **having, when separate, crystalline forms which are closely alike and being capable of forming homogeneous crystals containing varying proportions of the two ingredients,** are called **isomorphous substances** (Gk. ἴσος, equal; μορφή, form). Thus, potassium permanganate $KMnO_4$ and potassium perchlorate $KClO_4$ crystallize in the rhombic system, forming crystals with very similar angles (Fig. 53, p. 139), and when a solution containing both is allowed to evaporate there is formed but one set of crystals made up of both substances. Similarly, potassium iodide and ammonium iodide crystallize in cubes of the regular system, and, since all cubes are alike, necessarily show absolutely identical angles. In addition to this, however, they crystallize together from a solution containing both salts. Other pairs from amongst substances belonging to the regular system would not do this. The two salts are therefore isomorphous.

In the course of our study of the compounds of the metals we shall have occasion to note many examples of isomorphism. Thus the heptahydrates of the sulphates of many of the bivalent metals, such as $ZnSO_4,7H_2O$, $FeSO_4,7H_2O$, $MgSO_4,7H_2O$, etc., belong to the rhombic system, and form an isomorphous set of substances known as the *vitriols* (*q.v.*).

* In general, two substances which are absolutely unrelated may be deposited simultaneously from mixed aqueous solutions, but some of the crystals are pure specimens of one substance, and the rest are pure specimens of the other.

The alums (*q.v.*) also constitute an important set, and crystallize, separately and together, in the regular system (see, also, under Zinc sulphate). Amongst minerals, lead sulphide (PbS) and silver sulphide (Ag_2S) form a common isomorphous pair, and nearly all natural specimens of galena (*q.v.*) contain at least a little silver sulphide.

The chemical significance of isomorphism was at first exaggerated. Thus the elements magnesium and iron are not especially similar in their chemical relations, excepting that both are bivalent; yet they form several pairs of compounds which, like the sulphates (above), are isomorphous. Still, in practical chemical work a knowledge of the relations of a substance in respect to isomorphism is indispensable. It enables us to predict the probable impurities in a homogeneous-looking material, for non-isomorphous substances would have given a heterogeneous mixture with it. It assists us in separating and purifying chemical substances, for non-isomorphous substances can be separated by recrystallization from water (p. 273), or by washing with water or some other solvent (p. 276), at a temperature at which the solubilities of the substances are different (see Potassium nitrate). Isomorphous substances, however, can be separated only by conversion into some other form of combination in which the property is lacking. Thus, silver sulphide cannot be separated from lead sulphide by Pattinson's process (*q.v.*), and so the mixed metals, to the separation of which the process is applicable, must first be secured by reduction.

Some chemists regard isomorphous mixtures as solid solutions.

Exercises. — 1. Compare the electrical conductivities of normal sodium hydroxide and normal acetic acid with the conductivity of copper. What length of copper wire will present the same resistance as 1 cm. of each of these solutions when the cross-sections are alike?

2. What do we mean by saying that an oxide is strongly or feebly basic, or that it is acidic (p. 541)?

3. What is meant by the same terms when applied to an hydroxide?

4. Compare the molar solubilities at 18° (*a*) of the halides of silver and (*b*) of the carbonates and (*c*) oxalates of the metals of the alkaline earths, noting the relation between solubility and atomic weight.

5. What is the molar concentration of chloridion (*cf.* p. 149) in saturated solutions of silver chloride and lead chloride at 18°, assuming complete ionization in these very dilute solutions?

6. How does the behavior of complex acids, like chloroplatinic acid H_2PtCl_6, differ from that of acid salts?

CHAPTER XXXIII

THE METALS OF THE ALKALIES: POTASSIUM AND AMMONIUM

The Metals of the Alkalies. — The metals of this family form a homogeneous group, and there is a very general similarity between the properties of the corresponding compounds. Some of the physical properties of the elements themselves can be presented best in tabular form.

	AT. WT.	SP. GR.	M.-P.	B.-P.
Lithium	7.0	0.59	186°	above red heat.
Sodium	23.0	0.97	95.6°	742°
Potassium . . .	39.1	0.87	62.5°	667°
Rubidium . . .	85.5	1.52	38.5°	. . .
Caesium	132.9	1.88	26.5°	270°

It will be seen that the specific gravities of the elements increase with rising atomic weight, while the melting-points and boiling-points fall (*cf.* p. 410). A table including all the physical properties, both of the elements and their compounds, would show similar characteristics in a general way, with here and there noticeable irregularities such as that shown by the specific gravity of sodium.

The Chemical Relations of the Metallic Elements of the Alkalies. — The metals which are chemically most active are included in this group, and the activity increases with rising atomic weight, caesium being the most active positive element of all. A freshly cut surface of any of these metals tarnishes by oxidation as soon as it is exposed to the air. Indeed, there is scarcely time to see the metallic appearance in the case of potassium and the metals following it. All of these metals decompose water violently (*cf.* p. 97), liberating hydrogen. The hydroxides which are formed by this action are exceedingly active bases, that is to say, they give a relatively large concentration of hydroxidion in solutions of a given molecular concentration (p. 349).

Lithium hydroxide is the least active. In the dry form these hydroxides are not decomposed by heating, while the hydroxides of all other metals lose water more or less easily. All these metals seem to combine with hydrogen, lithium giving the most stable compound. The hydrides, however, unlike those of many of the non-metals, are not ionogens, and consequently do not give acids when dissolved in water. In all their compounds the metals of the alkalies are univalent.

The family may be subdivided into two minor groups. The compounds of potassium, rubidium, and caesium resemble one another closely, while those of sodium and lithium are sometimes largely divergent in physical properties. Thus, the chlorides of the potassium set, not only crystallize in cubes, but can form mixed crystals with one another in all proportions. They are isomorphous (*cf.* p. 545). The same is true of the bromides and of the iodides. Sodium chloride, although crystallizing in cubes likewise, does not form mixed crystals with the chlorides of the potassium set. In the case of lithium, the hydroxide is not nearly so soluble as are the hydroxides of the other metals, and the metal gives also an insoluble carbonate and phosphate, in which respect it resembles magnesium and differs from all the other members of the present group.

The compounds of ammonium will be discussed in connection with those of potassium, to which they present the greatest resemblance.

The solubilities are often decisive factors in connection with the preparation and use of salts. The reader will find most of these in the table on p. 544, or the diagram on p. 157, and, as a rule, the values will not be repeated in the descriptive paragraphs.

Potassium.

Occurrence. — Silicates containing potassium, such as feldspar and mica (p. 525), are constant constituents of volcanic rocks, and from the weathering of these rocks, and of the detritus formed from them which constitutes a large part of the soil, the potassium used by plants is obtained. These minerals are not used commercially as sources of potassium compounds. The salt deposits (see below) contain potassium chloride, alone (sylvite) and in combination with other salts, and most of the compounds of potassium are manufactured from this material. Part of our potassium nitrate, however, is purified Bengal saltpeter (p. 438). Potassium sulphate occurs also in the salt layers, and is used directly as a fertilizer.

Preparation. — Potassium was first made by Davy (1807) by bringing the wires from a battery in contact with a piece of moist potassium hydroxide. Globules of the metal appeared at the negative wire. This process has just come into use commercially, molten potassium chloride being the substance decomposed. The process which, during the intervening years, furnished potassium, was the heating of potassium carbonate with finely divided carbon in small retorts :

$$K_2CO_3 + 2C \rightarrow 2K + 3CO.$$

The vapor of the metal tends to combine with the carbon monoxide, forming an explosive compound $K_6C_6O_6$, and the yield is thus reduced. Castner's improved process involves the heating of potassium hydroxide with a spongy mass which is essentially a carbide of iron (CFe_2). The latter is made by heating together pitch and iron filings. No carbon monoxide is produced :

$$6KOH + 2C \rightarrow 2K_2CO_3 + 3H_2 + 2K.$$

Physical Properties. — Potassium is a silver-white metal which melts at 62.5°. It boils at 667°, giving a greenish vapor. The metal and its compounds confer a violet tint upon the Bunsen flame, and the spectrum (*q.v.*) shows characteristic lines.

Chemical Properties. — The density of the vapor shows the molecular weight of potassium to be about 40, so that the vapor is a monatomic gas. The element unites violently with the halogens, sulphur, and oxygen. In consequence of the latter fact it is usually kept under petroleum, an oil which neither contains oxygen itself, nor dissolves a sufficient amount of oxygen from the air to permit much oxidation of the potassium to take place.

The Hydride. — When hydrogen is passed over potassium heated to 360°, a hydride is formed. By washing the solid product with liquefied, dry ammonia the excess of potassium is removed and white crystals remain. These have the composition KH. On account of the ease with which it decomposes, the substance behaves much like potassium itself. When thrown into water, for example, it gives potassium hydroxide, and the hydrogen is liberated.

Potassium Chloride. — Sea-water and the waters of salt lakes contain a relatively small proportion of potassium compounds. During

the evaporation of such waters, however, the potassium compounds tend to accumulate in the mother-liquor while sodium chloride is being deposited. Thus, when the Salt Lake in Utah shall have finally dried up, the *upper* (last to be formed) part of the bed of salts which it will leave behind will contain layers rich in compounds of potassium. This condition is realized in geological deposits which have been formed in the same way. Thus, at Stassfurt, near Magdeburg, there is a thickness of more than a thousand meters of common salt, more or less mixed with and intersected by layers of sedimentary deposits. Above this are 25 – 30 meters of salt layers in which the potassium salts are chiefly found, while over all are several hundred meters of sandstone. Formerly the upper layers were simply stripped off and rejected. Now, however, the revenue obtained from the products of these layers is many times greater than that coming from the rock salt below.

The chief sources of the potassium chloride found in the salt beds are sylvite (KCl) and carnallite ($KCl, MgCl_2, 6H_2O$). The latter is heated with a small amount of water, or with a mother-liquor obtained from a previous operation and containing sodium and magnesium chlorides. The magnesium sulphate which it contains as an impurity remains undissolved. From the clear liquid, when it cools, potassium chloride is deposited first and then carnallite. The former is taken out and purified, and the latter goes through the process again. This potassium chloride is the source from which most of our potassium hydroxide and potassium carbonate, as well as salts of minor commercial importance, are made. It is a white substance crystallizing in cubes, melting at about 750°, and slightly volatile at high temperatures.

Potassium Iodide. — When iodine is heated in a strong solution of potassium hydroxide, the iodate and iodide are both formed (p. 277):

$$6KOH + 3I_2 \rightarrow 5KI + KIO_3 + 3H_2O.$$

The dry residue from evaporation is heated with powdered carbon to reduce the iodate, and all the iodide can then be purified by recrystallization. Another method of preparation consists in rubbing together iodine and iron filings under water. The soluble ferrous iodide (FeI_2) thus formed is then treated with additional iodine and gives a substance Fe_3I_8, intermediate in composition between ferrous and ferric iodides. This is also soluble. When potassium carbonate is added to the solution, a hydrated magnetic oxide of iron is precipitated, carbon

dioxide escapes, and evaporation of the clear solution gives potassium iodide:

$$Fe_8I_8 + 4K_2CO_3 + 4H_2O \rightarrow 8KI + Fe_8(OH)_8 + 4CO_2.$$

The salt forms large, somewhat opaque cubes (m.-p. 623°). It is used in medicine and for producing precipitates of silver iodide in photography. In the laboratory it is used whenever an iodide is required, for example, when experiments with iodidion are to be made

The Bromide and Fluorides. — Potassium bromide may be made in either of the ways used for the iodide. It crystallizes in cubes. It is used in medicine and for precipitating silver bromide in making photographic plates (*q.v.*). In the laboratory it is always employed when a bromide is needed as a source of bromidion.

The **fluoride** of potassium K_2F_2 may be obtained by treating the carbonate or hydroxide with hydrofluoric acid. It is a deliquescent, white salt. When treated with an equi-molecular quantity of hydrofluoric acid it forms potassium hydrogen fluoride KHF_2, a white salt which is also very soluble. This acid salt is used in the preparation of pure hydrofluoric acid, since the latter is liberated from it as a vapor at a high temperature.

Potassium chloride is the least soluble of the halides of potassium, the bromide, fluoride, and iodide coming next in that order. The position of the fluoride as the most soluble, when we should expect it to be the least soluble (p. 244), shows that this compound is somewhat exceptional. It is also slightly hydrolyzed by water, as if it were a salt of a dibasic acid (*cf.* p. 344). These facts, together with the existence of the acid fluoride, lead us to assign to it the formula K_2F_2. Other acid fluorides of the formulæ KH_2F_3 and KH_3F_4 have likewise been made. Since potassium, hydrogen, and fluorine are always univalent, and no ordinary valence is thus available for holding together groupings more complex than KF and HF, we may regard all these four fluorides of potassium as molecular compounds (p. 443).

Potassium Hydroxide. — This compound, known also as caustic potash and sometimes as potassium hydrate (p. 120), was formerly made entirely by boiling potassium carbonate with calcium hydroxide suspended in water (milk of lime):

$$K_2CO_3 + \uparrow Ca(OH)_2 \rightleftarrows CaCO_3 \downarrow + 2KOH.$$

The operation is conducted in iron vessels, because porcelain, being composed of silicates, interacts with solutions of bases. The action is, in theory, precisely similar to that of sulphuric acid upon barium dioxide (*cf.* p. 585). The potassium carbonate corresponds to the acid, being completely dissolved from the beginning, and the calcium hydroxide to the dioxide, since its relative insolubility enables the water to take up fresh portions into solution only when the part dissolved has already undergone chemical change. The calcium carbonate which is precipitated is much less soluble than the hydroxide, and hence the action goes forward. The action as a whole is reversible, for a reason which will be explained later (see Ionic equilibrium in Chap. xxxiv), and consequently such an amount of water is employed that the solution at no time contains more than about ten per cent of potassium hydroxide (sp. gr. 1.1). The conclusion of the action is recognized when a clear sample of the liquid no longer effervesces on addition of a dilute acid, and is therefore free from potassium carbonate.

Recently much potassium hydroxide has been manufactured by electrolytic processes. When a solution of potassium chloride is electrolyzed, chlorine is liberated at the anode, and hydrogen and potassium hydroxide at the cathode. The necessity of keeping those two sets of products apart, since by their interaction potassium hypochlorite and potassium chloride would be formed (*cf.* p. 266), has made the devising of suitable apparatus extremely difficult. In one type of apparatus a partition of asbestos cloth, especially prepared to resist the disintegrating effects of the alkali and the chlorine, divides the cell into two parts. In some cases this is placed vertically, and in others horizontally. In the latter case the anode is on the upper side of the partition, in order that the chlorine as it is liberated may ascend to the surface without stirring up the liquid or having occasion to pass near the partition. In all cases the anode is made of graphite, since this substance is less easily attacked by chlorine than is any other, and the cathode is made of iron, a metal which best resists the action of alkalies. The chlorine is used for making bleaching powder. Pure brine flows in continuously at one point, and a solution of the hydroxide containing much undecomposed chloride flows out at another.

The same process is applied to sodium chloride, and, in some factories, the apparatus is used solely for making bleaching materials, and most or all of the alkali is thrown away. This is on account of the cheapness of the caustic soda made by non-electrolytic processes, and

the expense involved in concentrating the rather dilute solution obtained electrolytically.

The Castner-Kellner apparatus (Fig. 97) employs a different principle very ingeniously for the separation of the products. The two end compartments are filled with brine and contain the graphite anodes. The central compartment contains potassium hydroxide solution and the iron cathode. The positive current enters by the anodes, and the chlorine is therefore attracted to and liberated upon the graphite. After rising through the liquid it is collected for the manufacture of liquefied chlorine or of bleaching powder. The ions of potassium or of sodium, as the case may be, are discharged upon a layer of mer-

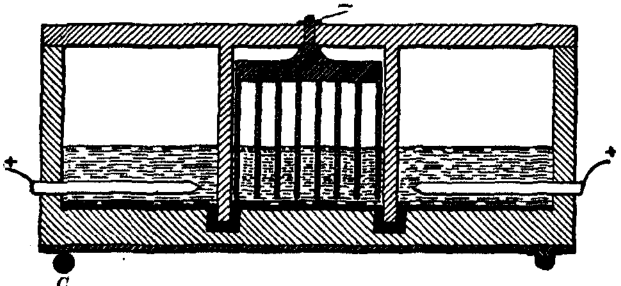


FIG. 97.

cury which covers the whole floor of the box, and the free metal dissolves in the mercury, forming an amalgam (p. 532). The layer of mercury extends beneath the partitions, and a slight rocking motion given to the cell by the cam (*C*) causes the amalgam to flow below the partition into the central compartment. Here the sodium leaves the mercury in the form of sodium ions and is attracted by the cathode. Upon this, hydrogen from the water is discharged, and the residual hydroxidion, together with the metallions, constitutes potassium or sodium hydroxide. A slow influx of salt solution at one point and overflow of the alkaline solution in the central cell at another, is maintained. The overflowing liquid contains 20 per cent of the alkali. Since in this form of the apparatus there is no undecomposed chloride present in the part of the solution which contains the hydroxide, simple evaporation to dryness furnishes the solid alkali.

Potassium hydroxide is exceedingly soluble in water, and consequently, instead of being crystallized from solution, the molten residue

from evaporation is cast in sticks. When, for chemical purposes, the hydroxide is required free from potassium carbonate and other impurities, it is dissolved in alcohol, in which the other substances are not soluble. Evaporation of this solution gives pure caustic potash. The hydroxide, in consequence of the very low vapor tension of its solution (*cf.* p. 162), is highly deliquescent. It also absorbs carbon dioxide from the air, giving potassium carbonate. This salt is itself deliquescent, and consequently a syrupy solution of the carbonate is the final result of weathering. Solutions of the hydroxide have an exceedingly corrosive action upon the flesh, decomposing it into a slimy mass by hydrolyzing the albuminous and other substances. In solution, the base is highly ionized, furnishing a high concentration of hydroxidion. Its aqueous solution is therefore used with salts of other metals for precipitation of less soluble bases. Commercially it is chiefly employed in the making of soft soap.

The Oxides. — The simple oxide K_2O may be made by heating potassium nitrate or nitrite with potassium in a vessel from which air is excluded: $KNO_3 + 5K \rightarrow 3K_2O + N$. It interacts violently with water, giving the hydroxide. When exposed to the air it unites spontaneously with oxygen, and K_2O_4 is formed.

When the metal burns in oxygen, K_2O_4, a yellow solid is the product. This substance interacts violently with water, giving potassium hydroxide, and the excess of oxygen is liberated. With perfectly dry oxygen, potassium does not unite, even when it is heated strongly.

Potassium Chlorate. — The preparation of this salt ($KClO_3$), by interaction of potassium chloride with calcium chlorate, has already been described (p. 273). It is also made by electrolysis of potassium chloride solution, the potassium hydroxide and chlorine which are liberated being precisely the materials required. All that is necessary is to use a warm, concentrated solution and to provide for the mixing of the materials generated at the electrodes. The salt crystallizes out when the solution cools.

Potassium chlorate crystallizes in monoclinic plates. It melts at about 359°, and at a temperature slightly above this the visible liberation of oxygen begins. Since heat is given out by the decomposition, the action may be almost explosive if large amounts of the material are employed. This decomposition doubtless takes place at all temperatures (p. 73), but below the melting-point the speed is so slight

that the phenomenon is not perceived. On account of the ease with which its oxygen is liberated, the salt is employed in making fireworks and as a component, along with antimony trisulphide, of the heads of Swedish matches. With acids it is used as an oxidizing agent on account of the chloric acid which is set free (p. 272). It is also employed in medicine.

Potassium perchlorate $KClO_4$, formed by the heating of the chlorate (p. 275), gives white crystals belonging to the rhombic system. Compared with the chlorate, on account of the greater difficulty in liberating its oxygen by heat, it finds little practical application.

The Bromate and Iodate. —These are the most familiar salts of their respective acids. The mode of their preparation has already been described (p. 277). Potassium iodate may be made also very conveniently by melting together potassium chlorate and potassium iodide at a low temperature. The iodate is much less soluble than the chloride, and the mixture may be separated by crystallization from water.

Potassium Nitrate. — The formation of this salt in nature and its mode of extraction and purification have already been described (p. 438). This source of supply proved insufficient, for the first time, during the Crimean war (1852–55), and a method of manufacture from Chili saltpeter (sodium nitrate), which is a much cheaper substance, was introduced. Sodium nitrate and potassium chloride are heated with very little water, and the sodium chloride produced by the action, which is a reversible one, is by far the least soluble of the four salts. On the other hand, at this temperature, the potassium nitrate is by far the most soluble. Hence the hot liquid drained from the crystals contains the required salt, and most of the sodium chloride is in the form of a precipitate. If the solubility curve of potassium nitrate (p. 157) is examined, it will be seen that this salt is but slightly soluble in cold water, and hence most of it is deposited when the solution cools. The crystals are mixed with little sodium chloride, for, as the curve shows, common salt is little less soluble at 10° than it is at 100°.

Potassium nitrate gives long prisms belonging to the rhombic system (Fig. 98). It melts at about 340°, and when more strongly heated gives off oxygen, leaving potassium nitrite (p. 449). Although it does not form a hydrate, the crystals inclose small portions of the mother-liquor, and consequently contain both water and impurities. When heated, the crystals fly to pieces explosively (**decrepitate**), on account of

the vaporization of this water. All substances which form large crystals and do not melt when warmed, behave in the same way and for the same reason. In consequence of this, the purest salt is made by violent stirring of the solution during the operation of crystallization, the result being the formation of a crystal-meal.

Potassium nitrate is used chiefly in the manufacture of **gunpowder**, which contains 75 per cent of the highly purified salt. The other components are 10 per cent of sulphur, 14 per cent of charcoal, and about 1 per cent of water. The ingredients are intimately mixed in the form of paste, and the material when dry is broken up and sifted, grains of different sizes being used for different purposes. The chemical action which takes place when gunpowder is fired in an open space probably results chiefly in the formation of potassium sulphide, carbon dioxide, and nitrogen :

$$2KNO_3 + 3C + S \rightarrow K_2S + 3CO_2 + N_2.$$

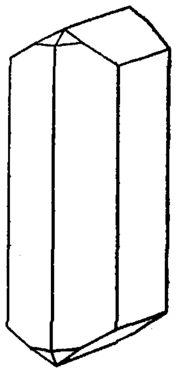


Fig. 98.

The explosion occurring in firearms follows a much more complex course, and half of the solid product is said to be potassium carbonate. The pressure, at the temperature of the explosion, if the gases could be confined within the volume originally occupied by the gunpowder, would reach about forty-four tons per square inch. In recent years common gunpowder has been displaced largely by **smokeless powder**, of which substances related to gun-cotton (p. 441) are the chief components.

Paper saturated with potassium nitrate solution and dried, is known as **touch-paper**. The salt interferes with the access of air to the cellulose, and the oxygen for the combustion is obtained from the nitrate. The product consequently does not blaze and cannot easily be blown out.

Formerly nitric acid was all made from potassium nitrate, but now the cheaper sodium nitrate is employed exclusively.

Potassium Carbonate. — This salt is manufactured from potassium sulphate, from the Stassfurt deposits, by the Le Blanc soda process (*q.v.*). A certain amount is also obtained from the fatty material, known as *suint*, which forms about 50 per cent of the weight of sheep's wool, and is separated from the latter by washing. When

this material, which contains the potassium salt of sudoric acid in large proportions, is calcined, potassium carbonate remains, and is extracted from the ash with water. Some plants, like the sugar-beet, take up exceptional quantities of potassium salts from the soil. The molasses remaining from the crystallization of beet-sugar (p. 500) is mixed with yeast and fermented. After the alcohol has been distilled off, the liquid, containing organic salts of potassium in solution, is evaporated, and the residue is ignited. In some districts potassium carbonate is still extracted from wood-ashes.

This salt is usually sold in the form of an anhydrous powder (m.-p. over 1000°). When crystallized from water it gives a hydrate $2K_2CO_3$, $3H_2O$. It is extremely deliquescent. Its aqueous solution has a marked alkaline reaction. The hydrolysis of the salt by the water is exactly analogous to that of sodium sulphide (p. 375), although not so extensive. The more elaborate scheme given in that connection may be put in simpler form to show that the action consists essentially in the formation of the ion HCO_3', by union of the ion CO_3'' with the hydrion of the water. This takes place because the ionization of the former ion is small enough to be commensurable with that of water itself: $CO_3'' + H^{\cdot} + OH' \rightarrow HCO_3' + OH'$. The commercial name of the substance is **pearl ash**. It is used in making soft soap and hard glass. It is also employed, by interaction with acids, in making salts of potassium.

When a concentrated solution of the salt is electrolyzed in such a way that the anode, towards which the KCO_3' ions travel, consists of a thin platinum wire, the crowding together of the discharged material results in the formation of the **percarbonate** (*cf.* p. 397):

$$2K\bar{C}O_3 + 2\oplus \rightarrow K_2C_2O_6.$$

The operation must be conducted between −15° and 0°. When the solution in the porous cell surrounding the anode is evaporated, the product is obtained as an amorphous bluish-white powder. The substance liberates oxygen when heated, and in other respects behaves like the persulphates. When it is treated with a dilute acid, a solution containing hydrogen peroxide is formed. The compound is therefore a mixed anhydride (p. 397) of hydrogen peroxide and potassium bicarbonate.

Potassium Cyanide. — Formerly this compound was made by heating potassium carbonate with nitrogenous animal matter. So

many other substances were formed at the same time, however, that the required product, which is very soluble, was difficult to isolate in a state of purity. It is now made by heating together potassium ferrocyanide (*q.v.*) and potassium carbonate. The ferrocyanide acts as if it were a mixture of potassium cyanide and ferrous cyanide: $K_4Fe(CN)_6 \rightarrow 4KCN + Fe(CN)_2$. The latter, by interaction with the potassium carbonate, would give potassium cyanide and ferrous carbonate, but this in turn, is decomposed by heat into ferrous oxide, which is insoluble, and carbon dioxide:

$$K_4Fe(CN)_6 + K_2CO_3 \rightarrow 6KCN + FeO + CO_2.$$

When the residue is extracted with water, only the potassium cyanide dissolves, and it is easily crystallized in pure form from the solution. Very interesting is the formation of potassium cyanide in the blast furnace (*q.v.*). Carbon and nitrogen unite at a very high temperature to form cyanogen (p. 260), and a sufficient amount of potassium is found in the materials to complete the production of the salt.

Potassium cyanide crystallizes in cubes. It is extremely soluble in water, and is therefore deliquescent. Its poisonous qualities are equal to those of hydrocyanic acid. The acid is so feeble as to be liberated even by the carbon dioxide of the air, and hence this salt always has a distinct odor of hydrocyanic acid. Potassium cyanide has a great tendency to form complex compounds with cyanides of other metals (*cf.* p. 536). Complex compounds of this kind are used in the galvanic deposition of silver and gold in commercial electroplating. Large amounts of the cyanide are also used in extracting gold (*q.v.*) from its ores, particularly in the Transvaal colony. The tendency to form complex compounds is doubtless connected with the fact that the cyanides are unsaturated compounds in which the carbon has two free valences: $K-N=C$ (p. 507).

Potassium cyanate $KCNO$ is made by heating potassium cyanide in the air, or, still better, with some easily decomposed oxide (p. 507). It is a white, easily soluble, crystalline salt.

Potassium thiocyanate $KCNS$ may be obtained by melting potassium cyanide with sulphur (*cf.* p. 508). It is a white, deliquescent salt which finds some applications in chemical analysis.

The Sulphate and Bisulphate. — The sulphate of potassium is a constituent of several double salts found in the Stassfurt deposits. It is extracted from **schoenite** $MgSO_4, K_2SO_4, 6H_2O$ and **kainite**

$MgSO_4, MgCl_2, K_2SO_4, 6H_2O$. The former is treated with potassium chloride and comparatively little water, whereupon the relatively insoluble potassium sulphate crystallizes out, and the magnesium chloride remains in the mother-liquor. The crystals belong to the rhombic system, contain no water of crystallization, and melt at 1066°. This salt is employed in large quantities in making potassium carbonate by the Le Blanc process and in preparing alum (*q.v.*). It is also much used as a fertilizer. Since plants take up solutions through their cell walls, they can absorb soluble compounds only. They are, therefore, dependent, for the potassium compounds which they require, upon the weathering out of soluble potassium compounds from the insoluble potassium silicates contained in the soil. The weathering takes place too slowly to furnish a sufficient supply for many crops, particularly that of the sugar-beet. Hence potassium sulphate is mixed directly with the soil. The mineral kainite itself is used for the same purpose.

Potassium hydrogen sulphate (bisulphate) $KHSO_4$ is made by the action of sulphuric acid upon potassium sulphate: $K_2SO_4 + H_2SO_4 \rightarrow 2KHSO_4$. It crystallizes from water, in which it is very soluble, in tabular crystals. When heated to about 200° it melts, and the elements of water are eliminated, the **pyrosulphate** remaining: $2KHSO_4 \rightarrow H_2O + K_2S_2O_7$. The latter, when still further heated, yields sulphur trioxide and potassium sulphate. The bisulphate is used in analysis for the purpose of decomposing oxides and silicates and converting them into sulphates. The substance is more efficient than sulphuric acid for this purpose, because the latter cannot be heated above 330°, while the liberation of the active sulphur trioxide from this salt takes place at a bright-red heat. The aqueous solution of the bisulphate is strongly acid on account of the considerable ionization of the hydrosulphanion.

Sulphides of Potassium. — By the treatment of a solution of potassium hydroxide with excess of hydrogen sulphide, a solution of **potassium hydrogen sulphide** is obtained. Evaporation of the solution gives a deliquescent solid hydrate $2KHS, H_2O$. When the solution, before evaporation, is treated with an equivalent amount of potassium hydroxide, and the water is driven off, the **sulphide** K_2S remains behind (*cf.* p. 375):

$$KHS + KOH \rightleftarrows K_2S + H_2O.$$

With proper care, the very soluble hydrate $K_2S, 5H_2O$ may be obtained. Considerable amounts of sulphur can be dissolved in solutions of either

of these sulphides. By evaporation of the resulting yellow liquids, various polysulphides have been obtained. To some of these have been ascribed the formulæ K_2S_3, K_4S_7, K_2S_4, K_4S_9, and K_2S_5 (*cf.* p. 376). Similar substances are produced, as a result of the liberation and recombination of sulphur, when the solutions are exposed to the oxidizing action of the air:

$$2KHS + O_2 \rightarrow 2KOH + 2S.$$

In most respects the corresponding compounds of potassium and sodium are similar in their physical properties and chemical action. Since, however, the latter are almost uniformly less expensive, they find much wider application. In a few cases, however, the potassium salt is more generally used. Thus, potassium chlorate and potassium iodide are much less soluble than the corresponding sodium compounds, and it is consequently possible in each of these two cases to separate by crystallization, and to purify the potassium salt with greater ease.

Properties of Kalion: Analytical Reactions.—The positive ionic material of the potassium salts is a colorless substance. It unites with all negative ions, and most of the resulting compounds are fairly soluble. For its recognition we add solutions containing those ions which give with it the least soluble salts. Thus, with chloroplatinic acid H_2PtCl_6 it gives a yellow precipitate of potassium chloroplatinate K_2PtCl_6. Since nearly one part of this salt dissolves in 100 parts of water, the test is far from being a delicate one. The solubility in alcohol is much smaller, and consequently the precipitate may frequently be obtained from a dilute solution by adding more than an equal volume of alcohol. Picric acid (p. 441) gives potassium picrate $KC_6H_2(NO_2)_3O$, which is much less soluble in water (0.4 parts in 100 at 15°). Perchloric acid and hydrofluosilicic acid likewise give somewhat insoluble salts of potassium. Potassium hydrogen tartrate $KHC_4H_4O_6$ is precipitated by the addition of tartaric acid to a sufficiently concentrated solution of a potassium salt. The normal tartrate $K_2C_4H_4O_6$ is much more soluble. It may be obtained by treating the precipitate with a solution of potassium carbonate or potassium hydroxide. Addition of an acid to this solution causes reprecipitation of the bitartrate.

The Spectroscope.—A much more delicate test for the recognition of a potassium compound consists in the examination by means of the

spectroscope of the light given out by a Bunsen flame, in which a little of the salt is held upon a platinum wire. When the amount of potassium is considerable, and no other substance which would likewise color the flame is present to mask the effect, the violet tint is recognizable by the eye. In general, however, the light must be analyzed.

White light is composed of vibrations of every wave-length within a certain range. If the light is made up of one or more wave-lengths only, it appears to the eye to be colored. Now, when a narrow bundle of rays of white light, coming through a slit, falls upon a three-sided prism standing with its edges parallel to the slit, the rays of various wave-length are retarded to different extents as they pass through the glass, and in consequence are bent from their paths by varying amounts. Fig. 99 shows a horizontal section through the slit (*S*) and prism, in which the width of the slit and of the beam of light are exaggerated. The light emerging at the other side of the prism consists, therefore, of a series of images of the slit arranged side by side. The red light is least refracted, and the red images of the slit, therefore, are most nearly in the same straight line with the original beam. The yellow, green, blue, and violet images are displaced more and more from this direction, and the resulting colored band is called a **spectrum**. The whole series of images of the slit may be received upon a screen, or directly upon an eye looking towards the prism. Now, when the light comes from the vapor of potassium heated in a Bunsen flame, there are produced, not thousands of images of the slit, representing as many different wave-lengths of light, but only two images, one red, and one deep blue, corresponding to the two wave-lengths which are alone contained in the original light. In a more powerful instrument other fainter lines are seen also. Naturally the brightness of all these lines is together equal to that of the original beam. No other substance gives any of those particular lines, although many others give blue and red light of somewhat different wave-lengths. Thus, strontium compounds give a blue light along with several red tints, but when strontium and potassium are used together, the lines are found not to be coincident. In the case of strontium, all the lines lie nearer to the yellow than in

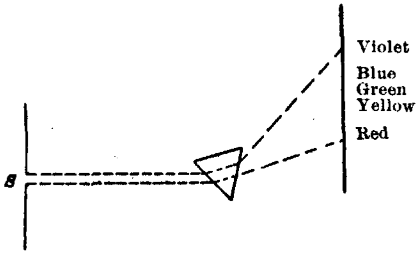


FIG. 99.

that of potassium. Since the whole light of the compound is thus concentrated in one or two narrow strips easily visible against a dark background, small amounts of the elements give effects which are readily recognizable in the instrument. This remains true even when, to the eye, the colors are completely obscured by the much more brilliant, yellow light which compounds of sodium produce. In the spectrum of sodium, this yellow light is all concentrated into two yellow lines which lie very close together.

Helium gives many lines, but one orange line (D_3), in particular, was noted in the spectrum of the sun's photosphere many years before the element was obtained from terrestrial sources by Ramsay. When the spectra of helium and other gases are to be examined in the laboratory, a little of the material is inclosed in a narrow, exhausted tube, through which an electrical discharge can be passed between platinum wires. Under this treatment helium shows its conspicuous orange line, and hydrogen a red and two blue ones. In this apparatus compounds are dissociated and give the spectra of their constituents. When a Bunsen flame is used with the salts* of metals, however, the temperature is not high enough to render visible the spectra of the non-metals contained in them. Indeed, even of the metals themselves, only the members of the alkali and alkaline-earth groups give distinct results.

Rubidium and Caesium.

Soon after the invention of the spectroscope by Bunsen and Kirchhoff, the instrument was applied to the examination of many substances. In 1860 Bunsen discovered several new lines in the spectrum given by materials derived from the salts in Dürkheim mineral water. Two new elements of the alkali group were found to cause their presence, and were named, from the colors of the lines which they gave, rubidium (red) and caesium (blue). Both elements have since been found in small quantities in various minerals. Rubidium is obtainable with relative ease from the mother-liquors of the Stassfurt works.

The metals may be obtained by heating their hydroxides with magnesium powder. The salts of these two elements are, in crystalline form and solubility, very much like those of potassium. In some cases the difference in solubility is sufficient to make separation possible. Thus, a mixture containing compounds of these two metals and of potassium gives with chloroplatinic acid a yellow precipitate,

* The chlorides are preferred because of their volatility. The salts of the oxygen acids are dissociated, and leave the highly involatile oxides (e.g. pp. 380, 444).

consisting of the three insoluble chloroplatinates. The solubilities at 10°, however, are as follows: Potassium chloroplatinate 0.9, rubidium chloroplatinate 0.15, caesium chloroplatinate 0.05. Hence, when the mixed precipitates are carefully washed with small quantities of cold water the potassium chloroplatinate can be almost entirely removed. On similar principles the two other metals can be separated from one another. The iodides of all three elements combine with iodine, giving tri-iodides (*cf.* p. 235), of which the tri-iodide of caesium is the most stable. Whether this is to be regarded as showing that the metals may occasionally be trivalent, or whether the extra iodine must be held to have entered into combination with the iodine of the compound, and not with the metal, has not been determined. In the parallel case of hydriodic acid, the union with extra iodine (p. 359) seems to show conclusively that iodidion can combine with iodine. While an inclination to trivalence in one of the metals of the alkalies would furnish a very acceptable link between the two sides of the first column in the periodic table (p. 411), since gold is a trivalent element, the latter of the two above assumptions is more probably the correct one.

AMMONIUM.

The compounds of ammonium claim a place with those of the alkali metals because in aqueous solution they give the ion $NH_4^{\cdot}$, an ion which in its behavior closely resembles kalion. Some of the special properties peculiar to ammonium compounds have been discussed in detail already (pp. 420, 421).

Ammonium Chloride. — This salt, known commercially as **salammoniac**, like all the other compounds of ammonium, is prepared from the ammonia dissolved by the water used to wash illuminating-gas (p. 418). It is purified by sublimation, and then forms a compact fibrous mass. It crystallizes from solution in cubes or octahedrons, which are often arranged according to a feathery pattern. When heated to 350° it volatilizes and is almost completely dissociated into ammonia and hydrogen chloride at this temperature (p. 421).

Ammonium bromide and **ammonium iodide** are white salts which crystallize in cubes or octahedrons, and are isomorphous with the corresponding potassium salts. They are dissociated by heat, and, in the case of the iodide, some of the hydrogen iodide is still further decomposed, giving free iodine.

Ammonium Hydroxide. — The nature and behavior of this substance have been fully discussed (p. 421). It may be remarked here that its very small basic activity as compared with that of potassium hydroxide is only in part due to the low degree of ionization of its molecules. A normal solution of ammonia contains much free NH_3, besides the NH_4OH produced by its union with water. Thus, some part of the material — how much we have at present no means of determining — is not actually in the form of a base and is not in directly ionizable condition at all. There are indications that the amount of uncombined ammonia may be considerable. Thus the organic derivative tetramethylammonium hydroxide $N(CH_3)_4OH$ is a very active base indeed, and one of the most conspicuous differences between it and ammonium hydroxide is that it cannot decompose into water and a non-ionizable substance. It is all available for ionization, while the material in ammonia-water is not.

Ammonium Nitrate. — This is a white crystalline salt which may be made by the interaction of ammonium hydroxide and nitric acid. When heated gently it decomposes, giving nitrous oxide and water (p. 450). It is used as an ingredient in fireworks and explosives. It exists in no fewer than four solid physical states. The melted salt solidifies at about 160°, giving crystals of the regular system. When these are allowed to cool somewhat, and are held at a temperature a little below 125.5°, they change gradually into a mass of rhombohedral crystals, the specific gravity and all other physical properties altering at the same time. This temperature is a transition point like that at which monoclinic sulphur assumes the rhombic form (p. 368). When these rhombohedral crystals, in turn, are held at a temperature a little below 83° they change their form once more into crystals which belong to the rhombic system and possess a third distinct set of physical properties. Finally, below 35° a fourth change, into rhombic needles, takes place, and this condition of the substance is the one familiar at ordinary temperatures. All these changes proceed in the reverse order when the temperature is elevated once more.

Ammonium Carbonate. — When ammonium hydroxide is treated with excess of carbon dioxide the solution gives, on evaporation, **ammonium bicarbonate** NH_4HCO_3. This is a white crystalline salt which is fairly stable at the ordinary temperature. It has, however, a faint odor of ammonia, and its dissociation becomes very rapid when

slight heat is applied. When a solution of this salt is treated with ammonium hydroxide, the neutral carbonate is formed:

$$NH_4HCO_3 + NH_4OH \rightleftarrows (NH_4)_2CO_3 + H_2O.$$

But this salt, when left in an open vessel, loses ammonia very rapidly, and leaves the bicarbonate behind.

The substance commonly sold as ammonium carbonate is the so-called **sesquicarbonate**, and is made by sublimation from a mixture of ammonium chloride or ammonium sulphate and chalk or powdered limestone. It is a mixture, in approximately equi-molar proportions, of ammonium bicarbonate and **ammonium carbamate**. The latter is a substance related to urea, and formed when ammonia and carbon dioxide gases are mixed:

$$2NH_3 + CO_2 \rightarrow O{=}C\begin{matrix}\diagup NH_2 \\ \diagdown O-NH_4.\end{matrix}$$

Ammonium cyanate is interesting on account of its rapid transformation, when warmed, into urea (p. 488). **Ammonium thiocyanate** NH_4NCS is a white salt which finds some application in analysis.

Ammonium Sulphate. — This is a white salt, crystallizing in rhombic prisms, which is used chiefly as a fertilizer. By eléctroylsis of a concentrated solution of the bisulphate, ammonium persulphate, which is less soluble, is formed and crystallizes out (*cf.* p. 397).

Sulphides of Ammonium. — When gaseous hydrogen sulphide and ammonia are mixed in equi-molar proportions and compressed or strongly cooled, **ammonium hydrogen sulphide** NH_4HS is formed as a crystalline deposit on the vessel. In an open vessel, at the ordinary temperature, this solid dissociates slowly into its constituents. The **sulphide**, $(NH_4)_2S$, can be produced under similar conditions by using twice as much ammonia. But it is much less stable and gives up half its ammonia, producing the acid sulphide very quickly. Solutions of these sulphides, made by passing hydrogen sulphide gas into ammonium hydroxide, are much used in analysis. The sulphide is almost completely hydrolyzed by water into the acid sulphide and ammonium hydroxide, its behavior being like that of sodium sulphide (p. 375):

$$\begin{matrix}2NH_3 + H_2S \rightleftarrows (NH_4)_2S \leftrightarrows 2NH_4^{\cdot} + S'' \\ H_2O \leftrightarrows OH' + H^{\cdot}\end{matrix}\Big\} \leftrightarrows HS'.$$

It is used for the precipitation of sulphides, such as zinc sulphide, which are insoluble in water. Although the S″ ions are not numerous at any moment, disturbance of the equilibrium by their removal, when they pass into combination, causes displacements which result in the generation of a continuous supply. The liquid smells strongly of ammonia and hydrogen sulphide on account of the dissociation of the parent molecules. Because of this dissociation the salt is preferred to potassium or sodium sulphide in analysis. The excess of the reagent can be driven out by simply boiling the mixture for a few minutes, all of the above equilibria being reversed. Another application in analysis depends on the tendency of this salt to unite with certain insoluble sulphides, particularly those of tin, arsenic, and antimony (*q.v.*), giving soluble complex salts.

The solution dissolves free sulphur, giving yellow polysulphides similar to those of potassium (p. 561). The same yellow substances are also obtained by gradual oxidation of ammonium sulphide when the solution of this salt is allowed to stand in a bottle from which the air is imperfectly excluded.

Microcosmic Salt. — This salt would be named, systematically, the tetrahydrate of secondary sodium-ammonium orthophosphate ($NaNH_4HPO_4, 4H_2O$). When ammonium chloride and ordinary sodium phosphate are mixed in strong solution the hydrate crystallizes out. The substance is used in bead tests (*cf.* pp. 467, 468).

Ammonium Amalgam. — As we have seen (p. 550), a potassium ion may be discharged and the element which it contains secured in the free condition. When a salt of ammonium is decomposed by electrolysis, however, the NH_4 ion upon its discharge gives ammonia and hydrogen, and no substance NH_4 is obtained. If, however, a pool of mercury is used as the negative electrode, the NH_4 forms an amalgam with it, and there seems to be no doubt that this substance is actually present in solution in the mercury. While the amalgam is being formed it swells up and gives off the decomposition products above mentioned, so that the existence of the substance is only temporary. The same material may be obtained by putting sodium amalgam into a strong solution of a salt of ammonium. The action is a displacement of one ion by another (p. 361):

$$\text{Na (diss'd in mercury)} + NH_4^{\cdot} \rightarrow NH_4 \text{ (diss'd in mercury)} + Na^{\cdot}.$$

This behavior is interesting since it is in harmony with the idea that ammonium, if it could be isolated, would have the properties of a metal. Substances, other than metals, are not miscible with mercury.

Ammonion: Analytical Reactions. — Ionic ammonium is a colorless substance. It unites with negative ions, giving salts, which, in the majority of cases, are soluble. Ammonium chloroplatinate, and to a less extent ammonium hydrogen tartrate, are insoluble compounds, and their precipitation is used as a test. The surest means of recognizing ammonium compounds, however, consists in adding a soluble base to the substance (*cf.* p. 421). The ammonium hydroxide, which is thus formed, gives off ammonia, and the latter may be detected by its odor. The quantity of the ammonium salt present may be determined by distilling the mixture and catching the distillate in a measured volume of normal hydrochloric acid. Determination of the amount of the acid remaining unneutralized, by titration with a standard alkali solution, then gives, by difference, the quantity of ammonium hydroxide.

Exercises. — 1. What kind of metals will, in general, interact with solutions of bases (*cf.* p. 553)?

2. Why should a mixture of potassium chlorate and antimony trisulphide be explosive?

3. How does the direct vision spectroscope differ from the arrangement here described (*cf.* any work on physics)?

4. Why is not ammonium carbamate (p. 566) formed by the neutralization method?

5. How should you set about making: a borate of potassium, potassium pyrophosphate, ammonium nitrite?

6. Why is the cleaning of platinum wires, as usually effected by holding them in the Bunsen flame, assisted by periodical dipping into hydrochloric acid (p.   )?

CHAPTER XXXIV

SODIUM AND LITHIUM. IONIC EQUILIBRIUM CONSIDERED QUANTITATIVELY

Sodium chloride forms more than two-thirds of the solid matter dissolved in sea-water, and the great salt deposits are largely composed of it. Sea-plants contain sodium salts of organic acids, just as land-plants contain potassium salts. Chili saltpeter, cryolite, and albite (a soda feldspar) are important minerals.

Preparation. — Sodium was first made by Davy (1807) by electrolysis of moist sodium hydroxide. It is manufactured by Castner's process, which is used also for potassium (p. 550), and by the electrolysis of fused sodium hydroxide by a method likewise invented by Castner. In the latter case the negative electrode projects through the bottom of the iron vessel containing the fused hydroxide. This electrode is surrounded by a wire-gauze partition, which is surmounted by a bell-shaped vessel of iron. The positive electrode is an iron cylinder surrounding the gauze. The sodium and hydrogen liberated at the cathode, being lighter than the fused mass, ascend into the iron vessel, under the edge of which the hydrogen escapes. Oxygen is set free at the anode.

Properties. — Sodium is a soft, shining metal, melting at 95.6° and boiling at 742°. The vapor is a monatomic gas. The metal is soluble in liquefied ammonia, giving a blue solution. The **amalgam with mercury**, when it contains more than a small amount of sodium, is solid, and probably contains one or more compounds of the two elements. This amalgam is often used instead of the metal sodium, since the dilution or combination with mercury makes the interactions of the metal more easily controllable. Sodium is used in the manufacture of many complex carbon compounds which are employed as drugs and dyes.

Sodium Hydride. — When hydrogen is led over sodium at 340° in such a way that the upper part of the tube is cooler, a matted mass of fine white crystals of the hydride is deposited on the cool part of

the tube. The temperature must not rise beyond 430°, since the compound dissociates rapidly at this temperature. The properties of the substance are similar to those of potassium hydride (p. 550).

Sodium Chloride. — Common salt is obtained from the salt deposits of Stassfurt, Reichenhall (near Salzburg), in Cheshire, at Syracuse and Warsaw in New York, at Salina in Kansas, in Utah, California, and many other districts. Natural brines are obtained from wells in various parts of the world. Since the salt can seldom be used directly, on account of impurities which it contains, it is purified by recrystallization from water. Natural brines, which are sometimes dilute, are often concentrated by dripping over extensive ricks composed of twigs. When the resulting brine is allowed to evaporate slowly by the help of the sun's heat, large crystals, sold as "solar salt," are obtained. By the use of artificial heat and stirring, smaller crystals of greater purity can be secured. Salt intended for table use must be freed from the traces of magnesium chloride (*q.v.*) present in the original brine or deposit, for this impurity causes it to absorb moisture more vigorously from the air. The purest salt for chemical purposes is precipitated from a saturated solution of salt by leading into it hydrogen chloride gas. Explanation of this effect will be given presently (see p. 584).

Common salt crystallizes in cubes, the faces of which are usually hollow. The crystals decrepitate (p. 556) when heated, and melt at about 820°. Common salt is the source of all sodium compounds, with the exception of the nitrate. From it come also most of the chlorine and hydrogen chloride used in commerce.

The Hydroxide and Oxides. — **Sodium hydroxide** is prepared both by the action of slaked lime upon sodium carbonate and by the electrolysis of a solution of sodium chloride, precisely as is potassium hydroxide (p. 554). An interesting method used at Niagara Falls, the Acker process, employs molten sodium chloride as the electrolyte and molten lead as the cathode. The sodium forms an alloy with the lead, which continually circulates along the trough-shaped cell and back beneath a partition. On issuing at one end it comes in contact with a jet of steam, and this removes the sodium from the lead, forming sodium hydroxide. The latter flows in the molten condition from the surface of the lead, and the metal returns to the trough.

Sodium hydroxide is a highly deliquescent substance, which, when

exposed to the air, first liquefies and then becomes solid on account of the formation of sodium carbonate. Its general chemical properties are identical with those of potassium hydroxide. It is used in the manufacture of soap, in the preparation of paper pulp, and in many other chemical industries.

Sodium peroxide Na_2O_2 is made by passing slices of sodium, resting upon trays of aluminium, through a tubular vessel. In this it comes in contact with a current of air which has been freed from carbon dioxide and is maintained at a temperature between 300° and 400°. This oxide when thrown into water decomposes in part, in consequence of the heat developed, giving sodium hydroxide and oxygen. With careful cooling, however, much of it can be dissolved. By interaction with acids it yields hydrogen peroxide. Sodium peroxide is now used commercially for oxidizing and bleaching. The ordinary **sodium oxide** Na_2O is made in the same way as is potassium oxide (p. 555).

The Nitrate and Nitrite. — The occurrence and purification of **sodium nitrate** have already been described (p. 438). Its crystals are of rhombohedral form (Fig. 9, p. 14). This salt is one of the best of fertilizers, since it furnishes to plants the nitrogen which they require in a very easily absorbed form. It is used also in the manufacture of potassium nitrate, of nitric acid, and of sodium nitrite.

Sodium nitrite is formed by heating sodium nitrate with metallic lead and recrystallizing the product (p. 449). Although very soluble it is less so than potassium nitrite, and is therefore more easily prepared in pure condition. It is used as a source of nitrous acid by manufacturers of organic dyes.

Manufacture of Sodium Carbonate. — Natural sodium carbonate is found in Egypt and in other parts of the world. At Owen's Lake, California, it is secured by solar evaporation of the water. The sesquicarbonate $Na_2CO_3,NaHCO_3,2H_2O$, being the least soluble of the carbonates of sodium, is the one deposited. Locally, small quantities of sodium carbonate are still made by the burning of sea-weed. Up to the close of the eighteenth century this was the only source of the compound, and the product from Spain, known commercially as *barilla*, was ten times as expensive as the carbonate now is. Hence glass and soap were proportionately dearer than at present.

In 1791 the French Academy offered a prize for the discovery of

an inexpensive method for the preparation of sodium carbonate from common salt, and **Le Blanc** proposed the process which bears his name and is still in use. During the Revolution his factory was destroyed, his patents were declared to be public property, and the inventor died by suicide. The chief stages of Le Blanc's process involve three chemical actions. In the first place, sodium chloride is treated with an equivalent amount of sulphuric acid in a large cast-iron or earthenware

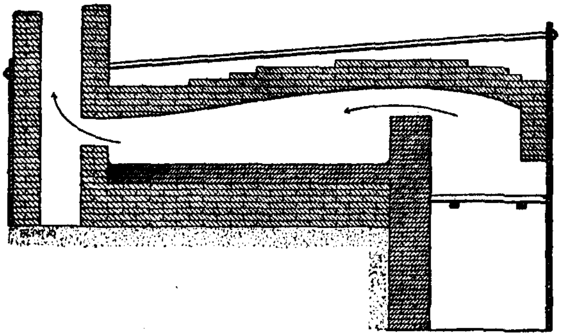


Fig. 100.

pan. The bisulphate thus produced (*cf.* p. 178), together with the unchanged sodium chloride, is raked out on to the hearth of a reverberatory * furnace (Fig. 100) and heated more strongly, while being continually worked by means of rakes, until the action is completed:

$$NaCl + NaHSO_4 \rightleftarrows Na_2SO_4 + HCl \uparrow.$$

The product of this treatment is called *salt-cake.* The hydrogen chloride, which is liberated in both stages, passes through towers containing running water in which it is absorbed. The second and third actions which follow are conducted in one operation. They consist in the reduction of the sodium sulphate by means of powdered coal and the interaction of the resulting sulphide of sodium with chalk or powdered limestone:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2,$$
$$Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS.$$

In the less modern factories the salt-cake, limestone, and coal are stirred upon the hearth of a reverberatory furnace and worked by hand.

* So called because the heated gases from the fire are *deflected* by the roof and play upon the materials spread on the bed of the furnace.

The material is finally collected into balls, and the end of the action is recognized by the fact that bubbles of carbon monoxide begin to force their way to the surface and cause little jets of blue flame. The gas is produced by the action of the coal upon the calcium carbonate, excess of both of these substances being present:

$$CaCO_3 + C \rightarrow CaO + 2CO.$$

The production of this gas gives a porous texture to the material, which facilitates the solution of the sodium carbonate in the final stage. The porous product is called *black-ash*. In modern factories hand labor is saved by giving the black-ash furnace the form of a rotating cylinder, in which projections from the walls assist in bringing about complete mixing of the materials during the action.

The black-ash varies very much in composition. It commonly contains 45 per cent of sodium carbonate, 30 per cent of calcium sulphide, 10 per cent of calcium oxide, and a number of other products and impurities. The coal used in the operation is selected so as to be as free as possible from combined nitrogen, the presence of which leads to the formation of cyanides.

Calcium sulphide is not very soluble in water, and is but slowly hydrolyzed by it (p. 376), especially when calcium hydroxide is present. The sodium carbonate is therefore extracted from the black-ash by a systematic treatment of the ash with water. The ash is placed in a series of vessels at different levels, and a stream of water flows from one vessel to another, until, when it issues from the last, it is completely saturated with sodium carbonate. A temperature of 30° to 40°, at which the solubility of sodium carbonate is at a maximum, is employed. When the material in the first of the vessels has been exhausted, the water is allowed to enter the second vessel directly, and a vessel containing fresh black-ash is added at the lower end of the series. In this way the most nearly exhausted ash comes in contact with pure water, which is in the best position to dissolve the remaining sodium carbonate rapidly, while the fresh black-ash encounters a solution already almost at the point of saturation.

The saturated solution is evaporated in shallow pans placed in the flues of the furnaces, and the monohydrate Na_2CO_3,H_2O, which crystallizes from the hot liquid, is raked out and dried by heat, leaving *calcined soda*. When this material is recrystallized from water and is allowed to deposit itself from the solution at the ordinary temperature, the decahydrate $Na_2CO_3,10H_2O$, *soda crystals* or *washing soda*, appears.

The solid residue from the extraction of the black-ash is known as *tank waste*, and contains 35–55 per cent of calcium sulphide. This material contains the sulphur of the original sulphuric acid, and its treatment involves a problem of some difficulty. If it is dumped near the factory the sulphur is lost, and by slow weathering yellow solutions containing polysulphides flow from the decomposing heap into the streams, and offensive odors of hydrogen sulphide fill the air. The most effective process for the recovery of the sulphur and consequent abatement of this nuisance is that of Chance. The product is arranged in a series of cylinders through which is passed carbon dioxide from a kiln of special form. The hydrogen sulphide liberated in the first cylinder forms the acid sulphide with the material contained in the second:

$$2CaS + CO_2 + H_2O \rightarrow Ca(SH)_2 + CaCO_3.$$

The further action of the carbon dioxide on this product gives, finally, a mixture of gases containing a larger proportion of hydrogen sulphide. By burning this mixture with a limited supply of air, the sulphur is then secured in free condition:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S.$$

About 70,000 tons of sulphur are thus recovered annually.

The **Solvay**, or **ammonia-soda process**, invented in 1860, is a serious rival of the Le Blanc process. It differs from the latter by involving almost nothing but ionic actions. A solution of salt containing ammonia and warmed to 40° fills a tower divided by a number of perforated partitions. Carbon dioxide, which is forced in below, makes its way up through the liquid. The ammonium bicarbonate formed by its action undergoes double decomposition with the salt, and sodium bicarbonate which is precipitated settles upon the partitions:

$NaCl + NH_4HCO_3 \rightleftarrows NaHCO_3\downarrow + NH_4Cl$, or $HCO_3' + Na^{\cdot} \rightleftarrows NaHCO_3\downarrow$.

The solid sodium bicarbonate, after being freed from the liquid, is heated strongly and leaves behind sodium carbonate:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O\uparrow + CO_2\uparrow.$$

The carbon dioxide which is liberated passes through the operation once more. The mother-liquor from the sodium bicarbonate contains ammonium chloride. This is decomposed by heating with quicklime, and the ammonia which is thus obtained is available for the treatment of another batch. The supply of carbon dioxide is generated in

lime-kilns of special form. The lime produced in these kilns serves for the liberation of the ammonia.

This process is cheaper than that of Le Blanc, and furnishes a much purer product. The latter process continues to be used, however, because of the hydrochloric acid which is produced at the same time. This finds remunerative application in the liberation of its chlorine for the manufacture of bleaching powder.

A possible rival of these two processes threatens to arise in the treatment of electrolytic sodium hydroxide with carbon dioxide gas.

Properties of Sodium Carbonate. — The common form of sodium carbonate consists of large monoclinic crystals of the decahydrate. This substance has a fairly high aqueous tension, and loses nine of the ten molecules of water which it contains when it is exposed in an open vessel. When warmed it melts at 35.2°, giving a solution of sodium carbonate in water. The residue from evaporation, above 35.2°, is the monohydrate. At higher temperatures, or with low atmospheric aqueous tension (p. 121), this in turn can be completely dehydrated (see Chap. xxxv). The decahydrate increases in solubility up to 35.2°, when it ceases to exist. Just above this temperature the monohydrate is the only substance which is stable. Its solubility is the same as that of the decahydrate at 35.2°, and diminishes as the temperature is raised. The relations are of the same nature as in the case of sodium sulphate (p. 158). In aqueous solution, sodium carbonate is hydrolyzed, and shows a marked alkaline reaction. The compound is used in large amounts for the manufacture of glass and soap, and is applied in innumerable ways in the scientific industries for purposes akin to cleansing.

Nearly all the familiar compounds of sodium are formed in the course of one or other of the processes by which sodium carbonate is manufactured, or are made by the treatment of sodium carbonate or sodium hydroxide with acids.

Sodium Bicarbonate. — This salt can be prepared in a state of purity by passing carbon dioxide over the decahydrate of sodium carbonate:

$$Na_2CO_3,10H_2O + CO_2 \rightleftarrows 2NaHCO_3 + 9H_2O.$$

The hydrate is spread upon a grating, through which the water generated by the action drips away. This action is reversible, and sodium bicar-

bonate shows, even in the cold, an appreciable tension of carbon dioxide. Even a solution of this salt gives off carbon dioxide, when boiled. An aqueous solution of pure sodium bicarbonate is neutral to phenolphthaleïn on account of the small degree of ionization of the ion HCO_3'. The salt is used in the manufacture of baking powder and in medicine.

Sodium Sulphate. — Anhydrous sodium sulphate (thenardite) crystallizes in the rhombic system, and is found in the salt layers. The same salt is contained in mineral waters, such as those of Friedrichshall and Karlsbad. It is formed in connection with the manufacture of nitric acid from sodium nitrate, and as an intermediate product in the making of sodium carbonate. Some of it is also prepared at Stassfurt by dissolving kieserite ($MgSO_4,H_2O$) in water along with sodium chloride. When the solution is cooled to 0°, the decahydrate of sodium sulphate crystallizes out, and magnesium chloride remains in solution.

The **decahydrate** of sodium sulphate, **Glauber's salt**, forms large monoclinic crystals which give up ten molecules of water when kept in an open vessel. When heated the crystals melt at 32.4°, and are resolved into the sulphate and water. The relations of the hydrate and anhydrous substance in respect to solubility have been fully discussed already (p. 158). When the decahydrate is mixed with concentrated hydrochloric acid, it is decomposed, and a part of the sulphate is converted into sodium chloride, the second action being a reversible one. This is one of those actions which proceed spontaneously, and therefore involve a diminution in the store of available energy in the system, although, so far as *heat* is concerned, a marked absorption of this form of energy takes place (*cf.* p. 27). The combination is used, in fact, as a freezing mixture.

Sodium Thiosulphate. — This salt is made by boiling a solution of sodium sulphite with sulphur. It is also obtained by boiling sulphur with caustic soda, and crystallizes from the mixed solution:

$$4S + 6NaOH \rightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O.$$

It gives large, transparent monoclinic crystals of a pentahydrate. When heated it first loses the water of hydration, and then decomposes, giving sodium sulphate, which is the most stable oxygen-sulphur compound of sodium, and sodium pentasulphide:

$$4Na_2S_2O_3 \rightarrow 3Na_2SO_4 + Na_2S_5.$$

From the latter, four unit-weights of sulphur can be driven by stronger heating. Sodium thiosulphate is used for fixing negatives in photography (*q.v.*), and by bleachers as antichlor (p. 396).

Phosphates of Sodium. — Common sodium phosphate is a dodecahydrate of the secondary orthophosphate, $Na_2HPO_4, 12H_2O$. It is made by neutralization of phosphoric acid with sodium carbonate, and crystallizes from the solution in large, transparent monoclinic prisms. Its properties have already been discussed (pp. 466, 467).

Sodium metaphosphate $NaPO_3$ is used for bead reactions (*cf.* p. 468).

Sodium Tetraborate. — This salt combines with ten molecules of water, forming large, transparent prisms, $Na_2B_4O_7, 10H_2O$. When heated it loses water, and leaves the easily fusible anhydrous salt in glassy form. Its sources have already been discussed under boric acid (p. 528). It is used as an ingredient in glazes for porcelain, in soldering, and for bead reactions (*cf.* p. 528).

Sodium Silicate. — A salt essentially of the composition of the metasilicate Na_2SiO_3 (*cf.* p. 522) is used for fire-proofing wood and other materials. Sand which is moistened with it and pressed in molds forms, after baking, a serviceable artificial stone. Since silicic acid is a feeble acid, this salt is much hydrolyzed, and gives a strongly alkaline solution (p. 523).

Properties of Natrion: Analytical Reactions. — Natrion is a colorless ionic material which unites with all negative ions. Practically all the salts so formed are soluble in water. The only ones which can be precipitated are sodium fluosilicate, made by the addition of hydrofluosilicic acid to a strong solution of a sodium salt, and sodium hydrogen pyroantimoniate $Na_2H_2Sb_2O_7$, made by similar addition of the corresponding potassium salt. For the recognition of natrion the solution is evaporated, and the residue examined with a spectroscope. If the yellow light persists longer than could be accounted for by the ordinary deposit of dust on the wire, a sodium compound is present in the material.

LITHIUM.

The compounds of lithium are made from amblygonite, a mixed phosphate and fluoride of aluminium and lithium. It occurs in lepidolite (a lithia mica) and in other rare minerals. Traces of compounds

of the element are found widely diffused in the soil, and are taken up by plants, particularly tobacco and beets, in the ashes of which the element may be detected spectroscopically.

The **metal** is liberated by electrolysis of the fused chloride, the manipulation being facilitated by the addition of some potassium chloride to lower the melting-point of the lithium salt. The melting-point and boiling-point of the free element are higher than those of any other alkali-metal, and the specific gravity (0.59) is lower than that of any other metal whatever. Lithium not only floats upon water, but also in the petroleum in which it is preserved.

The metal behaves towards water and oxygen like sodium (p. 548). It unites directly and vigorously with hydrogen (LiH), nitrogen (Li_3N), and oxygen (Li_2O), forming stable compounds. The chloride crystallizes in octahedra (p. 549). The relative insolubility (p. 544) of the hydroxide (LiOH), the carbonate (Li_2CO_3), and the phosphate ($Li_3PO_4,2H_2O$), is in sharp contrast to the easy solubility of the corresponding compounds of the other alkali-metals, and links lithium with magnesium. The compounds of lithium give a bright-red color to the Bunsen flame, and a bright-red and a somewhat less bright orange line are seen in the spectrum. The carbonate is used in medicine.

Ionic Equilibrium, Considered Quantitatively.

The Simple Case. — In view of the predominance of ionic actions in the chemistry of the metals, and of the determinative effect of ionic equilibria on many actions, it is essential that we should be prepared in future for a more exact study of these phenomena than we have hitherto attempted. The whole basis for this exact study has already been supplied, and only more specific application of the principles is demanded.

In the first place, the principles themselves must be recalled. When acetic acid, for example, is dissolved in water, it is ionized thus:

$$\underset{C_1}{HC_2H_3O_2} \rightleftarrows \underset{C_2}{H^{\cdot}} + \underset{C_3}{C_2H_3O_2{}'}.$$

The amount of molecular acetic acid dissociated per second in a given amount of the solution is proportional to the concentration of the molecules (C_1), while the amount of the two ionic materials, hydrion and acetanion, uniting to form molecules of acetic acid depends on the frequency of the encounters of the two kinds of ions and is propor-

tional to the ionic concentrations (p. 297). The unit of concentration (p. 250) is 1 mole per liter, or, in the present case, 60 g. of the acid, 1 g. of hydrion, and 59 g. of acetanion respectively, per liter, for these numbers represent the weight of one mole of each component. According to the law of concentration (p. 252):

$$\frac{C_2 \times C_3}{C_1} = \mathrm{K}, \qquad (1)$$

and the numerical value of this fraction, or of K, remains unchanged whatever the total concentration of the solution may be. If the solution is diluted, for example, C_2 and C_3 diminish relatively less quickly than C_1 in order that the value of the whole expression may remain the same. This is accomplished by ionization of a part of the material whose concentration is C_1 and its transference to the ionic forms whose concentrations are C_2 and C_3, respectively (p. 297).

A numerical example will show that this law of concentration expresses the facts with considerable exactness. The data in regard to acetic acid are as follows (p. 328):

Acetic Acid.	I. Molar Concentration.	II. Proportion of Whole Material Ionized.	III. Molar Concentrations of $H^{\cdot}$ (C_2) and of $C_2H_3O_2'$ (C_3). (I × II.)	IV. Molar Concentration of $HC_2H_3O_2$ (C_1). (I − III.)
Uni-molar .	1.0	0.004	0.004	1.0 − 0.004
Deci-molar .	0.1	0.013	0.0013	0.1 − 0.0013
Centi-molar .	0.01	0.0407	0.000407	0.01 − 0.000407

Now $C_2 = C_3$, since the ions are produced in equal numbers. Also, for our purpose, the numbers to be subtracted in column IV are relatively so small that the values 1, 0.1, and 0.01 may be taken to represent C_1 without appreciable error. Hence, substituting the data in equation (1) above, we have:

$$\frac{(.004)^2}{1} = .0_4160. \quad \frac{(.0013)^2}{.1} = .0_4169. \quad \frac{(.000407)^2}{.01} = .0_4165.$$

In other words, although the last solution is a hundred times more dilute than the first, and the degree of ionization has increased ten times, the whole expression remains close to the value 0.0_4165 and is essentially constant.

When conductivity data, like the above, are applied in the same way to the cases of more highly ionized substances, the values of K are less nearly constant. It is supposed that with this class of substances the measurements of degrees of ionization are less accurate, although the cause of the discrepancy has not been fully determined. However, in the very general applications of the data, which are all that we shall be required to make, the conclusions will not be affected by this fact.

The expression for ionic equilibrium in terms of concentration is often written in the following fashion:

$$\frac{[H^{\cdot}] \times [C_2H_3O_2']}{[HC_2H_3O_2]} = K.$$

Here $[H^{\cdot}]$ represents the molar concentration of hydrion (C_2), $[C_2H_3O_2']$ that of acetanion (C_3), and $[HC_2H_3O_2]$ that of molecular acetic acid (C_1). This form is more convenient for many reasons, and will be employed frequently.

Excess of One Ion. — When, through the presence of two substances with a common ion, C_2 is not equal to C_3, the above law (formula 1) still holds. For example, if with one mole of sodium acetate and one mole of acetic acid a single liter of solution is prepared, the solution will be uni-molar in respect to the acid and to the salt as well. Thus, *all* the acetanion will be available for uniting *both* with the hydrion and the natrion. Hence C_3, in the expression for the acetic acid equilibrium, will be abnormally large, and the ionization of the acid will be repressed. In uni-molar sodium acetate, 0.53 of the salt is ionized (p. 331), and, initially in the mixture of acid and salt, the concentration of acetanion will be .53 + .004 = .534, or nearly 134 times larger than in the acid alone. Hence, in order that the product $C_2 \times C_3$ may recover, as it must, a value much nearer to the old one, C_2 must be diminished to something like $\frac{1}{134}$ of its former magnitude. That is, C_2 will become equal to about 0.00003, the rest of the hydrion uniting with a corresponding amount of the acetanion to form molecular acetic acid. The effect of adding this amount of sodium acetate therefore is to reduce the concentration of the *hydrion* below the amount which can be detected by use of an indicator like methyl-orange. There is no less acetic acid present than before, but the number of acid ions is very much smaller.

This action is of course reciprocal, and the ionization of the sodium

acetate will be reduced also. But the acetanion furnished by the acetic acid is relatively so small in amount (.004 against .53) that the effect it produces on the ionization of the salt is imperceptible.

It will be noted that the acetanion and hydrion disappear in equivalent quantities, for they unite. There is, however, so much of the former that its loss goes unremarked, while there is so little of the latter that almost none of it remains. When substances of more nearly equal degrees of ionization are used, both effects are equally inconspicuous. Thus, sodium chloride and hydrogen chloride in uni-molar solutions yield approximately equal concentrations of chloridion (.784 and .676). Hence, if one mole of sodium chloride were to be dissolved in the portion of water already containing one mole of hydrogen chloride, the concentration of the chloridion, at a very rough estimate, would be nearly doubled. If this doubling of the concentration of chloridion almost halved that of the hydrion (.784), in order that the expression $[Cl'] \times [H'] \div [HCl]$ might remain constant, the concentration of the hydrion would still be about .400 and therefore 100 times as great as in molar acetic acid. It is thus altogether impossible to reduce the concentration of the hydrion given by an *active* acid like hydrochloric acid below the limit at which indicators are affected, for there is no way of introducing the enormous concentration of the other ion which the theory demands.

With more crude means of observation than indicators afford, effects like this may sometimes be rendered visible. This was the case with cupric bromide solution, to which potassium bromide was added (p. 335). The blue of the cuprion disappeared from view, while much cuprion was still present, because the brown color of the molecular cupric bromide covered it up completely.

Special Case of Saturated Solutions. — The commonest as well as the most interesting application of the conceptions developed above is met with in connection with saturated solutions, especially those of relatively insoluble substances.

The situation in a system consisting of the saturated solution and excess of the solute has been discussed already (p. 158). In the case of potassium chlorate, for example, we have the following scheme of equilibria:

$$KClO_3\ (\text{solid}) \rightleftarrows KClO_3\ (\text{diss'd}) \rightleftarrows K^{\cdot} + ClO_3'.$$

Solution of the solid is promoted by the solution pressure of the molecules, while it is opposed by the osmotic pressure of the dissolved

substance, and the solution is saturated when these tendencies produce equal effects (p. 152). Now it must be noted that the tendency directly opposed to the solution pressure is the *partial* osmotic pressure of the dissolved *molecules* alone. The chief contents of the solution, the molecules and two kinds of ions of the salt, and any foreign material that may be present, are like a mixture of gases, and the principle of partial pressure (p. 88) is to be applied. The ions and the foreign material do not deposit themselves upon the solid, and take, therefore, no part *directly* in the equilibrium which controls solubility. In respect to this the ions are themselves foreign substances. Hence the conclusion may be stated that **in solutions saturated at a given temperature by a given form** (p. 160) **of the solute, the concentration of the dissolved molecules considered by themselves will be constant whatever other substances may be present.**

The total solubility of a substance, as we have used the term hitherto, is made up of a molecular and an ionic part. The latter, as we shall presently see, is not constant when a foreign substance containing a common ion is already in the liquid. Since the treatment of the subject requires us now to distinguish between the two portions of the solute, a diagram (Fig. 101) will assist in emphasizing the distinction. The material at the bottom is the salt. The molecules and ions are to be thought of as being mixed and as being present in numbers represented by the factors *n* and *m*. Since no foreign body is present, the two ions in this case are equal in number.

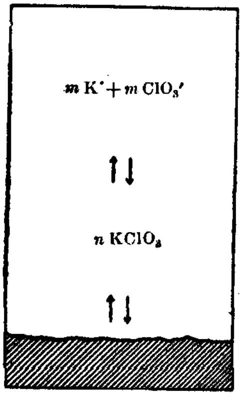


FIG. 101.

When we now apply these ideas to the mathematical expression of the relation:

$$\frac{C_2 \times C_3}{C_1} = K,$$

we perceive that, in a saturated solution, C_1, the concentration of the molecules is *constant*. Transposing, we have $C_2 \times C_3 = KC_1$. Hence the relation leads to the important conclusion that **in a saturated solution the product of the molar concentrations of the ions is constant**.

The practical bearing of this inference appears at once when we suppose an excess of one of the ions to be added, and remember that in chemical experiments mixtures of substances, including those with

common ions, are encountered much oftener than are pure solutions. If the original substance is not very soluble, and the values of C_2 and C_3 are therefore small, one may easily increase the value of C_3 a hundredfold by adding a material which is sufficiently soluble and sufficiently ionized. To preserve the value of the product $C_2 \times C_3$, the value of C_2 will then have to be diminished at once to one-hundredth of its former value. This can occur only by union of the ionic material it represents with an equivalent amount of that for which C_3 stands. The molecular material so produced will thus tend at first to swell the value of C_1. But the value of C_1 cannot be increased, for the solution is already saturated with molecules, so that the new supply of molecules, or others in equal numbers, **will be precipitated**. Hence the ionic part of the dissolved substance may be diminished, and the total solubility of the substance is seen to be in reality a variable quantity. We have actually precipitated a part of the dissolved material without introducing any substance, which, in the ordinary sense, can interact with it.

The product of the concentrations of the ions $C_2 \times C_3$ is called the **ion-product constant**, or **solubility product**, because these two values jointly determine the magnitude of the solubility of the substance. The solubility of the molecules is irreducible, but the ionic part of the dissolved material may become vanishingly small if the value of C_2 or C_3 is very minute. The ionic part of any particular substance is made up of the smaller of the two concentrations C_2 and C_3, plus an equivalent amount, and no more, of the other. The rest of the other is part of the solubility of some other component.

An Illustration: Potassium Chlorate. — A numerical example will show how this operates. The molar solubility of potassium chlorate at 18° is .52 (p. 544). At this concentration about .70 of the salt is ionized. The concentration of each ion is therefore .70 × .52 = .36. That of the molecules is .52 − .36 = .16. The solubility may therefore conceivably be reduced almost to .16 by admixture of a substance with a common ion, but cannot be carried below this value. The ionic product $C_2 \times C_3$, or $[K^{\cdot}] \times [ClO_3{}']$, is .36 × .36 = .13.

The molar solubility of sodium chlorate (p. 544), which is very soluble, is 6.4. When, to the saturated solution of the potassium salt, an equal volume of that of the sodium salt is added, some potassium chlorate (the less soluble substance) is at once thrown down :

$$\downarrow KClO_3 \leftrightarrows K^{\cdot} + ClO_3{}'.$$

Each solution is diluted by the volume of the other. The concentrations after mixing are therefore: $KClO_3$, .26; $NaClO_3$, 3.2. The degree of ionization of the potassium chlorate is diminished somewhat by the addition of the more concentrated sodium chlorate solution, that of the latter somewhat increased by the mixing with the more dilute potassium chlorate solution.* Leaving out of consideration the minor change in the degrees of ionization, the concentration of the $K^{\bullet}$ ions would be approximately $.70 \times .26 = .18$; that of the part of the ClO_3' ions coming from the potassium chlorate would be the same; that of the molecules $.26 - .18 = .08$. Of the sodium chlorate about .27 is ionized, so that the concentration of each of its ions is roughly $.27 \times 3.2 = .86$. Thus, the total concentration of chloranion is momentarily $.18 + .86 = 1.04$. The product $[K^{\bullet}] \times [ClO_3']$, $.18 \times 1.04$, is larger than .13, and so each of the factors will be reduced by an equal amount until the product equals .13. Leaving once more the changes in the degrees of ionization out of account, for our rough calculation, the equation $(.18 - x)(1.04 - x) = .13$ gives $x = .05$. Subtracting this quantity, we have the concentrations $.13 \times .99 = .13$ (nearly). That is to say, .05 moles per liter will be precipitated from *double* the original volume of the potassium chlorate solution, or .1 moles of the original .52 moles in the solution. Thus, roughly, the final disposition of the material originally present in one liter is:

Precipitated	.10 moles.
Remaining dissolved, molecular $.08 \times 2 =$	.16 moles.
Remaining dissolved, ionic . $.13 \times 2 =$	.26 moles.
	.52 moles.

Other Illustrations. — The precipitation of sodium chloride from a saturated solution, by the introduction of gaseous hydrogen chloride (p. 570), is to be explained in the same manner. A rough calculation, similar to that made above, would show, however, that the fraction of the whole material precipitated is smaller in the case of salt than in the case of potassium chlorate. This is because salt is much more soluble. With a substance even less soluble than potassium chlorate the effects are, conversely, relatively much greater.

* The degree of ionization of a salt (*e.g.* $KClO_3$) in mixtures of salts which all ionize with equal readiness, is approximately that which it would be in a pure solution of the salt ($KClO_3$) of a molar concentration equal to the total molar concentration of all the salts present. For example, in the above case, for potassium chlorate it would be that of a .26 + 3.2, or 3.46 molar solution, and for sodium chlorate it would be the same.

The evolution of a steady stream of hydrogen chloride is often accomplished by allowing concentrated sulphuric acid to flow into saturated hydrochloric acid (p. 182). The effect is due in part to repression of the ionization of the hydrogen chloride and elimination of molecules of the gas from the water which is already saturated with molecules of the same kind. The "salting out" of soap (p. 505) is another phenomenon similar to those described above (see p. 721).

Direction of a Chemical Change Determined by Ionic Concentrations. Rule for Precipitation or Solution of Insoluble Substances. — In discussing the manufacture of potassium hydroxide (p. 553), it was mentioned that the action of milk of lime on potassium carbonate is reversed when the concentration of the KOH becomes too great:

$$\left.\begin{array}{r} Ca(OH)_2(\text{solid}) \rightleftarrows Ca(OH)_2(\text{diss'd}) \rightleftarrows 2OH' + Ca^{\cdot\cdot} \\ K_2CO_3 \rightleftarrows 2K^{\cdot} + CO_3'' \end{array}\right\} \rightleftarrows \begin{array}{l} CaCO_3(\text{diss'd}) \rightleftarrows \\ CaCO_3(\text{solid}). \end{array}$$

The whole theory of the most common influences of ionic concentration may be illustrated by this one example.

We will imagine this action to be carried out at 18°, instead of 100°, since exact data in regard to the situation at the latter temperature are lacking. The molar solubility of calcium hydroxide at 18° is .02, and about .88 of the dissolved molecules are ionized.

Thus the molar concentration of the $Ca^{\cdot\cdot}$ ions is .88 of .02 or .0176. That of the OH' ions, since each molecule gives two of them, will be $2 \times .0176$, or .0352. The solubility product is $[Ca^{\cdot\cdot}] \times [OH']^2$, in which, when the substance is present by itself, the values are $.0176 \times (.0352)^2$.

Calcium carbonate is precipitated by the action and the liquid is therefore saturated with this salt. Its molecular solubility is .00013 (p. 544). In so dilute a solution we may regard the ionization as being complete. Hence the molar concentrations of $Ca^{\cdot\cdot}$ and of CO_3'' are each .00013. The solubility product of calcium carbonate is, therefore, $(.00013)^2$. Now the hydroxide at first furnishes $Ca^{\cdot\cdot}$ continuously with the concentration .0176, and the potassium carbonate, which is all dissolved from the beginning, gives CO_3'' in relatively high concentration. Thus both the ions of calcium carbonate are present in great excess, and this compound is precipitated rapidly. Leaving other matters out of consideration, we should expect the precipitation to go on until one or other of the ingredients was almost all used up and the product

$[Ca^{\bullet\bullet}] \times [CO_3'']$ had fallen to $(.00013)^2$. This presents the theory of *precipitation* in its relation to ionic concentration.

Further reflection shows, however, that, in this particular action, the hydroxidion continually accumulates in the solution. It begins at a concentration of .0352 and grows until it equals that of the kalion (whose concentration is constant throughout and need not be considered). The final result is a solution of potassium hydroxide. Let us consider the effect of this upon the dissolving of the calcium hydroxide:

$$\underset{}{Ca(OH)_2}\ (\text{solid}) \rightleftarrows \underset{C_1}{Ca(OH)_2}\ (\text{diss'd}) \rightleftarrows \underset{C_2}{Ca^{\bullet\bullet}} + \underset{C_3}{2OH'}.$$

When the potassium hydroxide has become di-molar, corresponding to the formation of an 11.2 per cent solution of caustic potash, .67 of its molecules are ionized, and therefore the concentration of hydroxidion is $2 \times .67$ or 1.34. In other words, one of the factors in the solubility product of calcium hydroxide has become very large. As we have seen, that product is normally constituted of the factors $.0176 \times (.0352)^2$ and equals $.0_4218$. Hence when the hydroxidion reaches .0352 + 1.34 or 1.3752, both factors must be reduced by an equal amount in order that the product may retain the value $.0_4218$. Thus $(.0176 - x)(1.3752 - 2x)^2 = .0000218$. Solving this cubic equation by trial, we find $x = .0175$. This gives the value of the concentration of the calcion, $.0176 - x = .0001$. The concentration of $Ca^{\bullet\bullet}$ is thus less than .00013, that given by calcium carbonate, and, if the potassium carbonate has by this time been exhausted, the concentration of $Ca^{\bullet\bullet}$ and CO_3'' will be smaller than those forming its solubility product, and this salt can no longer be precipitated. In fact, the precipitation may cease before so much as 11.2 per cent of potassium hydroxide has been formed.

It thus appears that the action goes forward because calcium carbonate is less soluble than calcium hydroxide, but, in presence of a sufficient concentration of potassium hydroxide, this relation will be reversed, calcium carbonate may dissolve and calcium hydroxide be precipitated. When the direction of an action is thus determined by a difference in solubility amongst slightly soluble substances, ionic concentrations may exercise a decisive influence on the result.

This illustrates the **rule** which describes the conditions under which **solution or precipitation proceeds: If the product of the molar concentrations of any pair of ions (one an anion, and one a cation) in a solution is *less* than the solubility product for the saturated solution of the**

substance formed by union of those ions, the substance, if present in excess, will dissolve. In the case just described this condition is fulfilled at first for $Ca(OH)_2$ and afterwards for $CaCO_3$. **Conversely, if the product of the concentrations of any pair of ions in a solution is greater than the solubility product for the saturated solution of the substance, the latter will be precipitated.** In the present instance, first $CaCO_3$ and then $Ca(OH)_2$ were the substances in this situation. This rule defines the conditions for all precipitations of ionogens in chemistry, and is therefore continually in application.

Exercises. — 1. The vapor density of sodium peroxide has not been determined. Why is the formula Na_2O_2 nevertheless assigned to it? What is its graphic formula?

2. Construct a scheme of equilibria (p. 371) showing the hydrolysis of calcium sulphide. Why does the presence of calcium hydroxide diminish the tendency to hydrolysis?

3. In terms of the principle stated on p. 587 explain the precipitation of insoluble hydroxides by the addition of a soluble hydroxide to a salt. What will be the effect of using an excess either of the salt or of the soluble hydroxide?

4. Calculate (p. 583) the effect of adding 2 volumes of a saturated (3.9 molar) solution of potassium chloride to a saturated (.52 molar) solution of potassium chlorate. Assume that 1.95 molar KCl is .71 ionized.

5. What will be the effect of adding a concentrated solution of silver nitrate to a saturated (p. 581) solution of silver sulphate.

CHAPTER XXXV

THE METALS OF THE ALKALINE EARTHS

The Chemical Relations of the Elements. — The metals of this group, calcium (Ca, at. wt. 40.1), strontium (Sr, at. wt. 87.6), and barium (Ba, at. wt. 137.4), constitute a typical chemical family both in the qualitative resemblance to one another of the elements and corresponding compounds and in the quantitative variation in the properties with increasing atomic weight. The metals themselves displace hydrogen vigorously from cold water, giving hydroxides. The solutions of these hydroxides, although dilute, on account of a rather small solubility, are strongly alkaline in reaction. The high degree of ionization of the hydroxides recalls the hydroxides of the metals of the alkalies, and their relative insolubility the hydroxides of the "earths" (*q.v.*).

In all their compounds, calcium, strontium, and barium are bivalent. The hydroxides are formed by union of the oxides with water, and, except in the case of barium hydroxide, are easily decomposed again by heating. The carbonates, when heated, yield the oxide of the metal and carbon dioxide, barium carbonate being the most difficult to decompose. The nitrates are broken up by heating and yield the oxide of the metal, nitrogen tetroxide, and oxygen. In these and other respects the compounds of the metals of the alkaline earths resemble those of the heavy metals and differ from those of the metals of the alkalies. Barium approaches the latter most nearly.

The table on p. 544 shows that the chlorides and nitrates of calcium, strontium, and barium are all soluble in water, the solubility diminishing in the order given. The sulphates and hydroxides cover a wide range from slight solubility to extreme insolubility. Of the sulphates, 2100, 110, and 2.3 parts, respectively, dissolve in one million parts of water. In the case of the hydroxides the order of magnitude is reversed, and the corresponding numbers are 200, 630, and 2200. The carbonates are almost as insoluble as is barium sulphate. The new element, radium (Ra, at. wt. 225), appears to belong to this family (see under Uranium).

CALCIUM.

Occurrence. — The fluoride, and the various forms of the carbonate, sulphate, and phosphate which are found in nature, are described below. As silicate, calcium occurs, along with other metals, in many minerals and rocks. It is found also in plants, and its compounds are important constituents of the bones and shells of animals.

The Metal.—Although the alkali metals can be liberated by heating the carbonates with carbon, the metals of the present family are not obtainable by this means. This may be due, in part, to imperfect contact between the materials in consequence of the infusibility of the oxides. Calcium is most easily made by electrolysis of the molten chloride. A hollow cylinder made of blocks of carbon bolted together and open above, forms the anode. A rod of copper hanging so that its end dips into the melt forms the cathode. The melting of the anhydrous calcium chloride with which the cylinder is filled is started by means of a thin rod of carbon laid across from the anode to the cathode. When the heat generated by the passage of the current through this highly resisting medium has melted a sufficient amount of the salt, the rod is removed, and the resistance of the fused material suffices to maintain the temperature. The calcium rises round the cathode and collects on the surface of the bath. By slowly elevating the copper cathode, the calcium, which adheres to it, may be drawn out of the fused mass in the form of a gradually lengthening, irregular rod. The rod of calcium is kept constantly in contact with the metal which accumulates on the surface, and thus forms one of the electrodes.

Calcium is a silver-white, crystalline metal (m.-p. 760°, sp. gr. 1.85) which is a little harder than lead, and can be cut, drawn, and rolled. It interacts violently with water. When dry and cold it is inactive, but when heated it unites vigorously with hydrogen, oxygen, the halogens, and nitrogen. It burns in the air, giving a mixture of the oxide and nitride. The presence of the latter may be shown by the liberation of ammonia when water is brought in contact with the residue:

$$Ca_3N_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2NH_3.$$

Calcium Hydride. — The hydride CaH_2, when formed by direct union of the constituents, is a white crystalline body. It interacts vigorously with water, liberating hydrogen.

Calcium Chloride. — Calcion is present in small amount in sea-water, and hence compounds containing calcium chloride, such as tachydrite $CaCl_2, MgCl_2, 12H_2O$, are found in salt deposits. The salt, for which there is no extensive commercial application, is formed in large quantities as a by-product in several industrial operations. Thus, it arises in the liberation of ammonia from ammonium chloride by the action of lime, in the manufacture of potassium chlorate (p. 273), and in the Solvay soda process (p. 574). By evaporation of any solution the hexahydrate of the salt, $CaCl_2, 6H_2O$, is obtained in large, deliquescent, six-sided prisms. On account of the great concentration of a saturated solution of this compound, the solid and solution do not reach a condition of equilibrium with ice (*cf.* p. 164) until the temperature has fallen to $-48°$. The freezing mixture must be made with the hydrate, and not with the anhydrous salt, as the latter gives out much heat in dissolving. The former, on the other hand, absorbs heat in liquefying, as all solids do.

There are several other hydrates of calcium chloride containing less than $6H_2O$, and those containing less water have lower aqueous tensions (*cf.* p. 122) than those containing more. By elevating the temperature, however, it is easy to raise the aqueous tension even of the monohydrate until it exceeds the partial pressure of water vapor in ordinary moist air, and so to drive out the water. To perform this rapidly, a temperature of over 200° is required. The dehydrated calcium chloride forms a porous mass which is used in chemical laboratories for drying gases and liquids. Usually the dehydration is left incomplete, as, at the temperature required to complete it rapidly, some interaction with the water occurs ($CaCl_2 + H_2O \rightarrow CaO + 2HCl$), and a little free alkali is present in the product. When calcium chloride is used as a drying agent, it is naturally able to reduce the partial pressure of the water vapor only to the value of the aqueous tension of the hydrate which is present, and no further. Even at low temperatures the aqueous tensions of hydrates are always perceptible (*cf.* p. 121). Concentrated sulphuric acid is a more thorough drying agent than calcium chloride, and phosphorus pentoxide, whose hydrated form (metaphosphoric acid) has no observable aqueous tension, is better still.

Calcium chloride forms molecular compounds, not only with water, but also with ammonia ($CaCl_2, 8NH_3$) and with alcohol. For drying these substances, therefore, quicklime is employed. Hydrogen sulphide interacts with the salt, giving hydrogen chloride, which renders the gas impure. This gas is therefore dried with phosphorus pentoxide.

Calcium Fluoride. — This compound occurs in nature as fluorite or fluor-spar CaF_2. It crystallizes in cubes, is insoluble in water, and when pure is colorless. Natural specimens often possess a green tint or show a violet fluorescence. It is formed as a precipitate when a soluble fluoride is added to a solution of a salt of calcium.

Fluorite is used in the etching of glass, as the source of the hydrogen fluoride (p. 241). It is easily fusible, as its name indicates (Lat. *fluere*, to flow), and is employed in metallurgical operations, for the purpose of lowering the melting-point (*cf.* p. 163) of the slag (*q.v.*), and so facilitating the separation of the latter from the metal.

Calcium Carbonate. — This compound is found very plentifully in nature. Limestone is a compact, indistinctly crystalline variety, while marble is a distinctly crystalline form. Chalk* is a deposit consisting of the calcareous parts of minute organisms; and egg-shells, oyster-shells, coral, and pearls are other varieties of organic origin.† A laminated kind of limestone found at Solnhofen is used for lithographic work. Calcite and Iceland spar (Ger. *spalten*, to split) are pure crystallized calcium carbonate. The former occurs in flat rhombohedrons, or in pointed, six-sided crystals (Fig. 52, p. 138) known as scalenohedrons ("dog-tooth" spar) belonging to the same system. All the crystals split with ease parallel to three planes of cleavage, giving rhombohedrons of the shape shown in Fig. 9 (p. 14), but this nearly cubical form is itself seldom found in nature. An entirely different crystallized variety is known as **aragonite**. This belongs to the rhombic system, although complex crystals ("twins") of hexagonal outline constitute the most familiar specimens. Aragonite, when heated strongly, resolves itself into a mass of minute crystals of calcite, and the latter is the more stable form of the substance. When calcium carbonate is produced by precipitation it is at first amorphous but slowly becomes crystalline. In cold liquids the resulting crystals are calcite; but in warm solutions the less stable form, that of aragonite, is first assumed.

When heated, calcium carbonate dissociates, giving carbon dioxide and quicklime:

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

At ordinary temperatures the decomposition is imperceptible. On the contrary, atmospheric carbon dioxide, in spite of its very low partial

* Blackboard "crayon" is usually made of gypsum and not of chalk.

† The hard coverings of crustacea and insects are not made of this substance, but of an organic material called chitin.

pressure, combines with quicklime, giving "air-slaked" lime. As the temperature rises, however, the tension of carbon dioxide coming from the carbonate increases, and has a fixed value for each temperature. If it is continually allowed to escape, so that the maximum pressure is not reached, the whole of the salt eventually decomposes. If, on the other hand, the gas is confined, the system reaches a condition of equilibrium. Attempts to increase the pressure on the gas beyond the dissociation pressure proper to the existing temperature, result in recombination. The phenomenon is precisely similar to the dissociation of barium dioxide (p. 257) and to the evaporation of a liquid (p. 117). The following data show the actual tensions at various temperatures:

Temperature	547°	625°	745°	810°	812°	865°
Tension in mm.	27	56	289	678	753	1333

Thus at 812° the pressure almost reaches one atmosphere, and at 865° it approaches two atmospheres.

Limestone is used in the manufacture of quicklime (*q.v.*) and of glass. It is employed largely as a flux in metallurgy, when minerals rich in silica are brought into fusible form by the production of calcium silicate ($CaSiO_3$). Large amounts also find application as building-stone.

The Phase Rule, a Method of Classifying all Systems in Equilibrium. — The formal resemblance that we have just shown to exist between the modes of behavior of a system composed of water and water-vapor in physical equilibrium, on the one hand, and of a system made up of calcium oxide, carbon dioxide, and undecomposed calcium carbonate in chemical equilibrium, on the other, is not a coincidence. A study of all kinds of systems in equilibrium shows that their different modes of behavior are limited in variety and can be classified in a very simple way.

The categories used for classification are: (1) the **independent components** in the system, and their number; (2) the distinct, physically separable parts or **phases** (p. 156) of the system, and their number; and (3) the **conditions** — temperature, pressure, and concentration (or volume) — and the degree of variability in the conditions which is possible without the occurrence of a change in the number of the phases.

The mode of employment of these three categories may be illustrated in the order of their mention:

1. In the water and water-vapor system, water is the *only component*. In the calcium carbonate system, the independent components are *two* in number, calcium oxide and carbon dioxide.

2. In the water and water-vapor system there are *two phases*, the liquid phase and the vapor phase. In the calcium carbonate system there are *three phases* — two solid phases, the carbonate and oxide, and one gaseous phase, the carbon dioxide.

3. In the water and water-vapor system either the temperature *or* the pressure may be altered, within certain limits, at will. But, whichever one of these two conditions it be that is thus changed, the preservation of the two phases will at once require a simultaneous modification in the other condition, of such a nature as will suit the new value of the first. Thus, if the pressure upon the vapor is raised, the vapor phase will be destroyed (p. 117) unless the temperature is simultaneously elevated to a certain definite point (p. 116). Similarly, if the temperature is raised, the liquid phase will all pass into vapor unless a sufficient increase in the pressure is simultaneously effected. There is therefore one, and only one degree of variability in the conditions — the system is **univariant**. By a study of the calcium carbonate system, as described above, it will be seen that it also is a univariant system.

A partial generalization of these results leads to the conclusion that when the number of the phases exceeds the number of the components by *one*, the system is univariant. Additional illustrations are now required for reaching a still more general statement.

If ice be added to the water and water-vapor system, and the system be allowed to reach equilibrium with all three phases present, we find on analyzing as before: one component (water), three phases (solid, liquid, and gaseous), and no variability in the system. *Neither* temperature *nor* pressure may be altered without ensuing disappearance of one or other of the three phases. This system is therefore **invariant**.

It thus appears that with an equal number of components, the more phases we have, the more restricted are the possibilities of change in the conditions. When the number of phases equals the number of components, the system is bivariant; when the number of phases exceeds the number of components by one, the system is univariant; when the number of phases exceeds the number of components by two, the system is invariant, and, in general,

Phases + Variable conditions = Components + 2.

The law, of which this equation is the most compact expression, is known as the **phase rule**, and was first formulated by Willard Gibbs, of Yale University. It applies to physical and chemical equilibria without distinction, and involves no consideration of molecular or other hypotheses.

Thus, the formal resemblance between the dissociation phenomena exhibited by calcium carbonate and other compounds, on the one hand, and the behavior of a liquid in contact with its vapor on the other, is due simply to the fact that in each case the number of phases exceeds the number of components by one. This will be found to hold in all cases where there is at each temperature a constant dissociation pressure. A decomposing hydrate, for example, furnishes such a case. The system is made up of one gaseous phase (water-vapor) and two solid phases (the hydrate, and the anhydrous substance or a lower hydrate). It has three phases and two components (water and the anhydrous substance), and is, therefore, univariant.

Again, when we have a sharp transition-point at a fixed temperature, that is, a unique temperature at which alone several different states of aggregation of a substance can co-exist (p. 115), the system is always invariant. Thus, ice and water (and vapor) co-exist at the melting-point of ice: three phases and one component. Again, two liquid forms of sulphur (p. 369) co-exist with sulphur vapor at 160°, which is the transition-point: three phases and one component as before. Still again, at 96° two solid forms of sulphur (p. 368) co-exist with sulphur vapor. In these cases the change which takes place at the transition point is purely *physical*. Analogous cases in which the change is a *chemical* one are equally familiar. The decahydrate of sodium carbonate decomposes (p. 575) above 35.2°. At this temperature the decahydrate and the monohydrate co-exist with the saturated solution and water-vapor: four phases and two components. The system is, therefore, invariant. The cases of gypsum (see p. 603) and sodium sulphate (p. 576) are similar.

Hard Water. — Calcium carbonate is almost insoluble in water. In the cold the solubility is a little over 1 part in 100,000; in hot water the solubility is even smaller. Water containing carbonic acid dissolves it more freely, on account of the formation of the more soluble calcium bicarbonate (*cf.* p. 482):

$$CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2.$$

A considerable excess of carbonic acid is required, as the action is markedly reversible. At 15° a liter of water saturated with carbon dioxide (at 760 mm. pressure) dissolves 0.385 g. of the carbonate, whereas a liter of pure water dissolves but .013 g. With a higher pressure of carbon dioxide still larger amounts may be dissolved. Conversely, when the carbon dioxide is driven out by boiling, the carbonate is reprecipitated.

Water containing salts of lime or magnesia in solution is known as **hard** water. The carbonate, which may be thrown down by boiling, gives "temporary hardness," while the sulphate of calcium, since it is soluble *per se* and is not affected by boiling, gives "permanent hardness." Soap will not produce a lather with hard water until the calcion has all been precipitated in the form of the calcium salts of stearic, palmitic, and oleic acids (p. 506). Commercially, the hardness is therefore measured by the quantity of a standard soap solution which is just sufficient to produce a persistent lather in a given amount of the water.

The temporary hardness may be removed by adding to the water a quantity of slaked lime sufficient to convert the excess of carbonic acid into calcium carbonate. The permanent hardness may be destroyed by the addition of sodium carbonate. In both cases the precipitated carbonate is allowed to settle or is separated by filtration.

When evaporated in steam-boilers hard water leaves behind a heavy deposit of boiler-crust containing all the salts formerly in solution. Similar water, when it dries slowly on the roofs of caverns, gives rise to stalactites. The drippings form stalagmites on the floors.

Calcium Oxide. — Pure oxide of calcium may be made by ignition of pure marble or calcite. For commercial purposes limestone is converted into quicklime in kilns. In the United States the "long-flame" process, in which the kiln is first charged with limestone and a fire is then kindled in a cavity left at the bottom, is the one most commonly used. Elsewhere, the limestone and coal are thrown, in alternate layers, into the kiln, and the products are withdrawn at the bottom. The latter, the "short-flame" method, demands less fuel, since the operation is continuous, and the structure is never allowed to cool, but the quicklime is mixed with the ash of the coal. In both cases a free passage of excess of air through the mass is desirable in order that, by reduction of the partial pressure of the carbon dioxide, the reverse action (p. 257) may be minimized. The better the ventilation, the lower the tempera-

ture at which rapid decomposition can be effected (*cf.* p. 592). The lowest temperature that will suffice is employed, as strong heating needlessly favors the interaction of the calcium oxide with the clay which most limestone contains. The product of the interaction with clay, calcium silicate, is fusible, and by closing many of the pores of the quicklime renders the subsequent slaking imperfect.

Pure calcium oxide is a white, porous solid. It is infusible even in the oxyhydrogen flame, but may be melted and boiled in the electric arc. It is not reducible by sodium, or by carbon excepting at the temperature of the electric furnace.

Calcium Hydroxide. — When water is poured upon quicklime it is first absorbed into the pores mechanically. The chemical union by which the hydroxide is formed:

$$CaO + H_2O \rightleftarrows Ca(OH)_2,$$

proceeds slowly. When it is complete the product is a fine powder occupying a much larger volume than the original materials. The action is accompanied by the development of much heat, and during its progress a part of the water is driven off as steam. The action is reversible, and at a high temperature the hydroxide can be dehydrated. Quicklime from pure limestone slakes easily, and is known as "fat" lime. That made from material containing clay or magnesium carbonate is "poor" lime. The latter slakes slowly and often incompletely, and, when used for mortar, does not harden so satisfactorily.

Calcium hydroxide is slightly soluble in water, 600 parts of water dissolving 1 part of the hydroxide at 18°, and about twice as much water being required at 100°. The solution, relatively to its concentration, is strongly alkaline. On account of its cheapness, this substance is used by manufacturers in almost all operations requiring a base, and it thus occupies the same position amongst bases that sulphuric acid does amongst acids. When the presence of much water is unnecessary or undesirable, a suspension of the solid hydroxide in the saturated solution ("milk of lime"), or even a paste, is employed. In such cases, as in the manufacture of caustic alkalies (p. 585), the action takes place with the part which is at the moment in solution, and proceeds through the continual readjustment of a complex set of equilibria. Some of the industries in which caustic lime plays a part are: the manufacture of alkalies, bleaching powder, and mortar, the removal of the hair from hides in preparation for tanning, and the purification of illuminating-gas (p. 513).

Mortar and Cement.—Mortar is made by mixing water with slaked lime and a large proportion of sand. The "hardening" process consists in an interaction of the carbon dioxide of the air with the calcium hydroxide:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O.$$

After the superficial parts have been changed, the process goes on very slowly, and many years are required before the deeper layers have been transformed. The minute crystals of calcium carbonate which are formed are interlaced with the sand particles, and a rigid mass is finally produced. The sand is useful in two ways. In the first place, it makes the whole material more porous, and so facilitates the diffusion of the gas into the interior. In the second place, since the sand is not itself altered, its presence prevents the formation of large cracks which would otherwise arise from the shrinkage that accompanies the formation of the carbonate. The "hardening" does not begin until the excess of water used in making the mortar has evaporated, and hence ordinary mortar is unsuitable for use in damp places such as cellars.

Cement is made by strongly heating a mixture of limestone, clay, and sand, and pulverizing the product. Some natural limestones, containing over 20 per cent of clay, give cements without the addition of other ingredients. When the cement is mixed with water, it gradually sets to a solid mass which appears to consist of a mixture of silicates of calcium and aluminium. The change proceeds throughout the whole material simultaneously, since it is not dependent on access of any gas, and not, as in the case of mortar, from the surface inwards. For this reason the hardening of cement occurs just as well under water as in any other locality.

Calcium Oxalate.—This salt may be observed under the microscope in the cells of many plants. It appears in the form of needle-shaped or of granular crystals. Since it is the least soluble salt of calcium, its formation is used as a test for calcium ions. Calcium is estimated quantitatively by adding ammonium oxalate to the neutral or slightly alkaline solution of the calcium salt. The precipitate is separated by filtration, washed with water, and then heated strongly (**ignited**) in a crucible. The product weighed is calcium oxide, $CaC_2O_4 \rightarrow CaO + CO_2 + CO$. More often, perhaps, the oxalate is ignited with sulphuric acid, and the calcium weighed as sulphate.

Interaction of Insoluble Salts with Acids, Resulting in Solution of the Salt. — It was noted above that for the complete precipitation of calcium oxalate a neutral solution must be used. The salt passes into solution when in contact with acids, especially active acids. Thus, with hydrochloric acid, it gives calcium chloride and oxalic acid, both of which are soluble:

$$CaC_2O_4 \uparrow + 2HCl \rightleftarrows CaCl_2 + H_2C_2O_4. \qquad (1)$$

The action of acids upon insoluble salts is so frequently mentioned in chemistry and is so important a factor in analytical operations that it demands separate discussion. The present case is a typical one and may be used as an illustration.

According to the rules already explained (p. 587), calcium oxalate (or any other salt) is precipitated when the product of the concentrations of the two requisite ions $[Ca^{\cdot\cdot}] \times [C_2O_4'']$ exceeds the solubility product for a saturated solution of calcium oxalate in pure water. If we assume complete ionization, this value in the present instance (p. 544) will be $[0.0_443] \times [0.0_443]$. When, on the contrary, the product of the concentrations of the two ions falls below the limiting value, a condition which may arise from the removal in some way either of the $Ca^{\cdot\cdot}$ or of the C_2O_4'' ions, the undissociated molecules will ionize, and the solid will dissolve to replace them until the ionic concentrations necessary for equilibrium with the molecules have been restored or until the whole of the solid present is consumed. Now an ion may be removed in two ways. It may combine with another ionic material to form either (1) a still more insoluble substance, or (2) a substance which although soluble is less highly ionized than the original salt. The former of these causes determined the solution of calcium hydroxide and precipitation of calcium carbonate in the manufacture of potassium hydroxide (p. 586). Here it is the other cause which comes into operation. The oxalanion from the calcium oxalate combines with the hydrion of the acid (usually an active one) which has been added, and forms molecular oxalic acid:

$$C_2O_4'' + 2H^{\cdot} \leftrightarrows H_2C_2O_4. \qquad (2)$$

Hence dissociation of the dissolved molecules of calcium oxalate proceeds, being no longer balanced by encounters and unions of the now depleted ions, and this dissociation in turn leads to solution of other molecules from the precipitate.

It will be seen that this second plan for the removal of ions will be

successful only when the new acid is a feebly ionized one. Here, to be specific, the concentration of the C_2O_4'' in the equilibrium (2) above must be less than that of the same ion in a saturated calcium oxalate solution. Now oxalic acid does not belong to the least active class of acids. Its ionization is chiefly into $H^{\bullet}$ and HC_2O_4', as is usual with dibasic acids, but the latter ion is broken up to an appreciable extent into $H^{\bullet}$ and C_2O_4''. There is, however, a decisive factor in the situation which we have not yet taken into account. The hydrochloric acid which we used for dissolving the precipitate is a very highly ionized acid and gives an enormously greater concentration of hydrion than does oxalic acid. Hence the hydrion is in excess in equation (2), and the condition of equilibrium for oxalic acid, $\frac{[H^{\bullet}]^2 \times [C_2O_4'']}{[H_2C_2O_4]} = K$ in this particular case, will be satisfied by a correspondingly small concentration of C_2O_4''. The whole change, therefore, depends for its accomplishment not only on the mere presence of hydrion, but on the repression of the ionization of the oxalic acid by the great excess of hydrion furnished by the active acid that has been used. As a matter of fact, we find that a weak acid like acetic acid has scarcely any effect upon a precipitate of calcium oxalate. An acid stronger than oxalic acid must be employed. The whole scheme of the equilibria is as follows:

$$\left.\begin{array}{l} CaC_2O_4\,(\text{solid}) \leftrightarrows CaC_2O_4\,(\text{diss'd}) \leftrightarrows Ca^{\bullet\bullet} + C_2O_4'' \\ \qquad\qquad 2HCl \qquad\qquad \leftrightarrows 2Cl' + 2H^{\bullet} \end{array}\right\} \rightleftarrows H_2C_2O_4\,(\text{diss'd}). \quad (3)$$

When excess of an acid sufficiently active to furnish a large concentration of hydrion is employed, the last equilibrium is then driven forward and the others follow. With addition of a weak acid, only a slight displacement occurs, and the system comes to rest again when the molecular oxalic acid has reached a sufficient concentration.

A **generalization** may be based on these considerations: **an insoluble salt of a given acid will in general interact and dissolve when treated with a solution containing another acid, provided that the latter acid is a more highly ionized (more active) one than the former** (see below). This principle furnishes one of the means of measuring the relative activity of different acids, for the more active the acids the larger will be the amount of the insoluble salt (say calcium oxalate) which equal quantities of equivalent solutions will decompose.

Even active acids frequently fail to bring salts of weak acids into solution, especially when the weak acid is itself present also. Here the cause lies in the fact that such salts are less soluble than those of

the calcium oxalate type, and give so low a concentration of the negative ion that the utmost repression of the ionization of the corresponding acid does not give a lower value for the concentration of this ion than does the salt itself. Thus we have seen (p. 375) that even hydrochloric acid (dilute) will not dissolve a number of sulphides. For example, in the case of cupric sulphide in presence of excess of hydrogen sulphide, the S″ factor in the solubility product $[Cu^{\cdot\cdot}] \times [S'']$ remains smaller than that in the scheme defining the hydrogen sulphide equilibrium $\frac{[H^{\cdot}]^2 \times [S'']}{[H_2S]}$ even when the S″ factor in the latter is diminished in consequence of great addition of hydrion. In this case the first link in the chain of equilibria:

$$\left.\begin{array}{l} CuS\ (solid) \leftrightarrows CuS\ (diss'd) \leftrightarrows Cu^{\cdot\cdot} + S'' \\ \qquad\qquad\qquad 2HCl \qquad\quad \leftrightarrows 2Cl' + 2H^{\cdot} \end{array}\right\} \rightleftarrows H_2S\ (diss'd),$$

tends so decidedly backward that only the use of concentrated acid will increase the concentration of the $H^{\cdot}$ to an extent sufficient to secure any marked advance of the whole action. We must add, therefore, to the above rule: **provided also that the salt is not one of extreme insolubility**. This point will be illustrated more fully in connection with the description of individual sulphides (see under Cadmium).

Illustrations of the application of these generalizations are countless. Carbonic acid is made from marble (p. 480), hydrogen sulphide from ferrous sulphide (p. 371), hydrogen peroxide from sodium peroxide (p. 303), and phosphoric acid from calcium phosphate (p. 456). In each case the acid employed to decompose the salt is more active than the acid to be liberated. On the other hand, calcium phosphate (except when freshly precipitated) and calcium oxalate are insoluble in acetic acid because this acid is weaker than are phosphoric and oxalic acids. We have thus only to examine the list of acids showing their degrees of ionization (p. 330) in order to be able to tell which salts, if insoluble in water, will be dissolved by acids, and, in general, what acids will be sufficiently active in each case for the purpose. In chemical analysis we discriminate between salts soluble in water, those soluble in acetic acid (the insoluble carbonates and some sulphides, for example), those requiring active mineral acids for their solution, and those insoluble in all acids.

The influence of solubility is shown not only by the sulphides, but also, for example, by the sulphates. Thus, barium sulphate is not ap-

preciably dissolved even by the most active acids (p. 390), being a salt of a rather highly ionized acid, and being itself very insoluble. Yet calcium sulphate, being much less insoluble (p. 544), is dissolved to a noticeable extent by the same acids.

Phosphates, oxalates, and other insoluble salts of weak acids, when they have been dissolved by active acids, are reprecipitated on addition of a basic solution. The hydroxyl combines with the hydrion of the acid, and so removes the agent by whose influence solution was effected. Hence, in analysis, the phosphates of barium, strontium, calcium, and magnesium are dissolved by acids and are reprecipitated by ammonium sulphide (an alkaline substance), along with the iron group.

Precipitation of Insoluble Salts in Presence of Acids. — The **converse of solution**, namely, **precipitation**, depends upon the same conditions: **an insoluble salt which is dissolved by a given acid cannot be formed by precipitation in the presence of this acid.** Thus, calcium oxalate can be precipitated in presence of acetic acid but not in presence of active mineral acids in ordinary concentrations. Cupric sulphide or barium sulphate can be precipitated in presence of any acid, but ferrous sulphide and calcium carbonate in the absence of acids only.

Dissolving of Insoluble Salts by Solutions of Salts. — The effect of **salt solutions on insoluble salts** is seldom very marked. The dissolving of salts by acids depends, as we have seen, ultimately upon the wide differences in degree of ionization which characterize acids. Now, salts are nearly all highly ionized substances, and therefore the same drastic effects in the way of solution of insoluble substances are not to be expected. In making this statement, we are purposely leaving the formation of complex ions out of consideration since it will be taken up later (see Copper). So far as the simple crosswise exchange of ions is concerned, and of this nature have been all the cases so far considered, the effect of adding a solution of a salt to a precipitate is simply to produce a very limited amount of dissolved un-ionized molecules of two new salts. This change does not usually consume much of the insoluble material. Thus, calcium carbonate with sodium chloride solution will give a little of the molecular forms of calcium chloride and sodium carbonate:

$$Ca^{\cdot\cdot} + 2Cl' \leftrightarrows CaCl_2 \text{ and } 2Na^{\cdot} + CO_3'' \leftrightarrows Na_2CO_3,$$

and a very little of the insoluble carbonate will dissolve. It is only when the insoluble salt is of the less insoluble class that the effects are

otherwise than negligible. Thus, calcium sulphate is somewhat more soluble in many solutions of salts than it is in water.

Calcium Carbide. — The manufacture of this compound has been described (p. 478), and the formation of acetylene by its interaction with water has already been discussed (p. 496). The substance was discovered by Wöhler in 1862, was first prepared by the use of electrical heating by Borchers in 1891, and was made on a large scale in 1892 by Wilson, a Canadian engineer.

Bleaching Powder. — This substance (*cf.* p. 266) is manufactured by conducting chlorine into a box-like structure containing slaked lime spread upon perforated shelves. When the transformation is complete, the supply of the gas is shut off, and some lime-dust is blown into the chamber to absorb the remainder of the free chlorine. The action is represented by the equation already given, or by the following:

$$2Ca(OH)_2 + 2Cl_2 \rightarrow CaCl_2 + Ca(OCl)_2 + 2H_2O.$$

While pure lime should thus yield a product containing 49 per cent of chlorine, in practice the proportion is always less. Good bleaching powder should contain 36–37 per cent of chlorine.

That bleaching powder is a mixed salt CaCl(ClO) rather than an equi-molar mixture of calcium chloride and calcium hypochlorite, which would have the same composition, is rendered probable by the facts that the material is not deliquescent as is calcium chloride, and that calcium chloride cannot be dissolved out of it by alcohol.

Bleaching powder is somewhat soluble in water, and in solution the ions $Ca^{\bullet\bullet}$, Cl', and ClO' are all present. Addition of acids causes the formation of hydrochloric and hypochlorous acids. The oxidizing and, incidentally, the bleaching properties (p. 269) of the latter are characteristic of the acidified liquid. Weak acids like carbonic acid displace the hypochlorous acid only (*cf.* p. 267), and hence the dry powder, when exposed to the air, has the odor of the latter substance rather than that of chlorine.

The substance is largely used by bleachers (*cf.* p. 270), and as a disinfectant to destroy germs of putrefaction and disease.

Calcium Nitrate. — This salt is found in the soil (p. 438), and may best be prepared in pure form by treating marble with nitric acid and allowing the product to crystallize from the solution. Calcium

nitrate forms several hydrates. The tetrahydrate $Ca(NO_3)_2, 4H_2O$, which forms transparent monoclinic prisms, is the one deposited at ordinary temperatures. The anhydrous salt is easily soluble in alcohol. It is used in the laboratory for drying nitrogen peroxide. When heated it decomposes (*cf.* p. 444), giving nitrogen peroxide, oxygen, and quicklime.

Calcium Sulphate. — This salt is found in large quantities in nature. The mineral anhydrite $CaSO_4$ occurs in the salt layers (see under Manganous sulphate). It contains no water of crystallization, and its crystals belong to the rhombic system. The dihydrate, $CaSO_4, 2H_2O$, is more plentiful. In granular masses it constitutes alabaster. When perfectly crystallized it is named gypsum or selenite. The same hydrate is formed by precipitation from solutions. Its solubility is about 1 in 500 at 18°. Its solubility varies in an unusual manner with temperature, increasing slowly to 38° and then falling off.

When its temperature is raised, the dihydrate quickly shows an appreciable aqueous tension. After three-fourths of the water has escaped, a definite hydrate $(CaSO_4)_2, H_2O$ remains. This hemihydrate shows a much smaller tension of water vapor (*cf.* p. 122).

The transition temperature at which the dihydrate passes sharply into the hemihydrate is 107°. It corresponds to the temperature of 35.2° at which the decahydrate of sodium carbonate turns into the monohydrate and water. At 107° both of the hydrates are in equilibrium with water (p. 594). Naturally this state of affairs can be realized only in a tube sealed up to prevent the escape of the water.

Plaster of paris is manufactured by heating gypsum until nearly all the water of hydration has been driven out. When it is mixed with water, the dihydrate is quickly re-formed and a rigid mass is produced. If, in course of manufacture, the water is all removed, or the temperature is allowed to rise much above the most favorable one (about 125°), the product when mixed with water does not set quickly and is said to be "dead-burnt." In explanation of this it should be noted that natural anhydrite combines very slowly with water. Apparently good plaster of paris must contain some unchanged particles of the dihydrate which may act as nuclei. They fulfil the same rôle as the crystal which is added to a supersaturated solution (p. 159), without which crystallization may be long delayed or may even fail to take place. Probably with moderate heating the product is a mixture of the dihydrate and the hemihydrate with anhydrous salt, while the

more rapid decomposition at higher temperatures destroys all of the first. The former mixture must be an unstable system, and the dihydrate loses water to the anhydrous salt. At ordinary temperatures, however, this transference must be very slow, and hence the property of setting is not lost by prolonged storage.

That the plaster sets, instead of forming a loose mass of dihydrate, is due to the fact that the anhydrous salt is more soluble than the dihydrate, and so a constant solution of the one and deposition of the other goes on until the hydration is complete:

$$\left.\begin{array}{l} CaSO_4\ (\text{solid}) \rightleftarrows CaSO_4\ (\text{diss'd}) \\ \qquad\qquad\qquad 2H_2O \end{array}\right\} \rightleftarrows CaSO_4, 2H_2O\ (\text{solid}).$$

This process results in the formation of an interlaced and coherent mass of minute crystals.

Plaster of paris is used for making casts and in surgery. The setting of the material is accompanied by a slight increase in volume, and hence a very sharp reproduction of all the details in the structure of the mold is obtained. An "ivory" surface, which makes washing practicable, is conferred by painting the cast with a solution of paraffin or stearine in petroleum ether. The waxy material, left by evaporation of the volatile hydrocarbons, fills the pores and prevents solution and disintegration of the substance by water. Stucco is made with plaster of paris and rubble, and is mixed with a solution of size or glue instead of water.

Calcium Sulphide. — This compound is most easily made by strongly heating pulverized calcium sulphate and charcoal. The sulphate is reduced:

$$4C + CaSO_4 \rightarrow CaS + 4CO.$$

Calcium sulphide is meagerly soluble in water, but is nevertheless slowly dissolved in consequence of its decomposition by hydrolysis into calcium hydroxide and calcium hydrosulphide (*cf.* p. 375). It is probable that the action would be less nearly complete than it is if the reverse action were not weakened by the precipitation of the calcium hydroxide:

$$2CaS + 2H_2O \leftrightarrows Ca(OH)_2 \downarrow + Ca(SH)_2.$$

Since calcium sulphide is thus decomposed by water it cannot be precipitated from aqueous solution by adding a soluble sulphide, such

as ammonium sulphide, to a solution of a salt of calcium. Only the soluble hydrosulphide can be formed.

Ordinary calcium sulphide, after it has been exposed to sunlight, usually shines in the dark. Barium sulphide behaves in the same way. On this account these substances are used in making luminous paint. They apparently owe this behavior to the presence of traces of compounds of vanadium and bismuth, for the purified substances are not affected in the same fashion.

Phosphates of Calcium. — The **tertiary orthophosphate of calcium** $Ca_3(PO_4)_2$, known as phosphorite, is found in many localities. It is probably derived from the remains of animals. Guano contains some of the same substance, along with compounds of nitrogen. Apatite, $3Ca_3(PO_4)_2,CaF_2$, a double salt with calcium fluoride, is a common mineral and frequent component of rocks. The orthophosphate forms about 83 per cent of bone-ash, and is contained also in the ashes of plants. It may be precipitated by adding a soluble phosphate to a solution of a salt of calcium.

Since it is a salt of a weak acid, and belongs to the less insoluble class of such salts, calcium phosphate is dissolved by dilute mineral acids (*cf.* p. 598), the ions HPO_4'' and H_2PO_4' being formed. When a base, such as ammonium hydroxide, is added to the solution, the calcium phosphate is reprecipitated (*cf.* p. 601).

Calcium phosphate is chiefly used in the manufacture of phosphorus and phosphoric acid (p. 456), and as a fertilizer. The supply of calcium phosphate in the soil arises from the decomposition of rocks containing phosphates, and is gradually exhausted by the removal of crops. Bone-ash is sometimes used to make up the deficiency. It is almost insoluble in water, however, and, although somewhat less insoluble in natural water containing salts like sodium chloride (*cf.* p. 601), is brought into a condition for absorption by the plants too slowly to be of much service. In consequence of this the "superphosphate" (see below) is preferred.

Primary calcium orthophosphate is manufactured in large quantities from phosphorite by the action of sulphuric acid. The unconcentrated "chamber acid" is used for this purpose, as water is required in the resulting action. The amounts of material employed correspond to the equation:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 6H_2O \rightarrow Ca(H_2PO_4)_2,2H_2O + 2CaSO_4,2H_2O.$$

As soon as mixture has been effected, the action proceeds with evolution of heat, and a large cake of the two hydrated salts remains. This mixture, after being broken up, dried, and packed in bags, is sold as "superphosphate of lime." The primary phosphate which it contains is readily soluble in water, and is therefore of great value as a fertilizer.

Calcium Silicate. — Calcium metasilicate $CaSiO_3$ forms the mineral wollastonite, which is rather scarce, and enters into the composition of many complex minerals, such as garnet, mica, and the zeolites. It may be made by precipitation with a solution of sodium metasilicate (p. 577), or by fusing together powdered quartz and calcium carbonate or quicklime:

$$SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2.$$

Glass. — Common glass is a complex silicate of sodium and calcium, or a homogeneous mixture of the silicates of these metals with silica. It has a composition represented approximately by the formula $Na_2O, CaO, 6SiO_2$, and is made by melting together sodium carbonate, limestone, and pure sand:

$$Na_2CO_3 + CaCO_3 + 6SiO_2 \rightarrow Na_2O, CaO, 6SiO_2 + 2CO_2.$$

For the most fusible glass, a smaller proportion of quartz is employed. This variety is known as **soda-glass**, or, from its easy fusibility, as **soft glass**. First, the materials are heated to a temperature high enough to produce chemical action without bringing about complete melting. This permits the ready escape of the gases. Then the temperature is raised to about 1200° until fusion is complete and all the bubbles have escaped. Finally, the crucible and its contents are allowed to cool to 700–800° to allow the latter to acquire the viscosity required for working.

Plate-glass is made by casting the material in large sheets and polishing the surfaces until they are plane. Window-glass is prepared by blowing bulbs of long cylindrical shape, and ripping them down one side with the help of a diamond. The resulting curved sheets are then placed on a flat surface in a furnace and are there allowed to open out. Beads are made, chiefly in Venice, by cutting narrow tubes into very short sections and rounding the sharp edges by fire. Ordinary apparatus is made of soft soda-glass, and hence when heated strongly it tends to soften and also to confer a strong yellow tint (*cf.* p. 563) on the flame.

In all cases the articles are annealed by being passed slowly through a special furnace in which their temperature is lowered very gradually. Glass which has been suddenly chilled is in a state of tension and breaks easily when handled.

Bottles are made with impure materials, and owe their color chiefly to the silicate of iron which they contain. In making cheap glass, sodium sulphate is often substituted for the much more expensive carbonate. In this case powdered charcoal or coal is added to reduce the sulphate:

$$2Na_2SO_4 + C + 2SiO_2 \rightarrow 2Na_2SiO_3 + CO_2 + 2SO_2.$$

Soft glass is partially dissolved by water. When powdered glass is shaken with water the solution soon dissolves enough sodium silicate to give the alkaline reaction (pink color) with phenolphthaleïn (*cf.* p. 355).

Bohemian, or **hard glass**, is much more difficult to fuse than soda-glass, and is also much less soluble in water. It is manufactured by substituting potassium carbonate for the sodium carbonate, and is used for making apparatus for special purposes where infusibility or insolubility are desirable. When lead oxide is employed instead of limestone, a soda-lead glass known as **flint glass** is produced. This has a high specific gravity, and a great refracting power for light, and is employed for making glass ornaments. By the use of grinding machinery, **cut glass** is made from it. It is easily fusible, and dissolves in water like soda-glass.

Colored glass is prepared by adding small amounts of various oxides to the usual materials. The oxides combine with the silica, and produce strongly colored silicates. Thus, cobalt oxide gives a blue, chromium oxide or cupric oxide a green, and uranium a yellow glass. Cuprous oxide, with a reducing agent, and compounds of gold, give the free metals, suspended in colloidal solution in the glass, and confer a deep-red color upon it. Milk-glass contains finely powdered calcium phosphate in suspension, and white enamels are made by adding stannic oxide.

Glass is a typical amorphous substance (*cf.* p. 139). From the facts that it has no crystalline structure, and that it softens gradually when warmed, instead of showing a definite melting-point, it is regarded as a supercooled liquid of extreme viscosity. Most single silicates crystallize easily, and have definite freezing- (and melting-) points. Glass may be regarded as a solution of several silicates. When kept for a

considerable length of time at a temperature insufficient to render it perfectly fluid, some of its components crystallize out, the glass becomes opaque, and "devitrification" is said to have occurred. The absence of such changes in cold glass may be attributed to that general hampering of all molecular movements and interactions which is characteristic of low temperatures. The word "crystal" popularly applied to glass is thus definitely misleading.

Calcion: Analytical Reactions. — Ionic calcium is colorless. It is bivalent, and combines with negative ions. Many of the resulting salts are more or less insoluble in water. Upon the insolubility of the carbonate, phosphate, and oxalate are based tests for calcion in qualitative analysis (see below). The presence of the element is most easily recognized by the brick-red color its compounds confer on the Bunsen flame, and by two bands — a red and a green one — which are shown by the spectroscope (p. 561).

STRONTIUM.

The compounds of strontium resemble closely those of calcium, both in physical properties and in chemical behavior.

Occurrence. — The carbonate of strontium $SrCO_3$ is found as strontianite (Strontian, a village in Argyleshire), and is isomorphous with aragonite. The sulphate, celestite $SrSO_4$, is more plentiful. It shows rhombic crystals, which are isomorphous with those of anhydrite, often have a blue color, and are commonly associated with native sulphur in specimens from Sicily. The metal may be isolated by electrolysis of the molten chloride.

Compounds of Strontium. — The compounds are all made from the natural carbonate or sulphate. The former may be dissolved directly in acids, and the latter is first reduced by means of carbon to the sulphide, and then treated with acids.

Strontium chloride, made in one of the above ways, is deposited from solution as the hexahydrate. The **nitrate** comes out of hot solutions in octahedrons which are anhydrous. From cold water the tetrahydrate is obtained (see under Manganous sulphate). The anhydrous salt is mixed with sulphur, charcoal, and potassium chlorate to make "red fire." The **oxide** SrO may be secured by igniting the car-

bonate, but on account of the low dissociation tension of the compound it is obtained with greater difficulty than is calcium oxide from calcium carbonate. It is generally made by heating the nitrate or hydroxide.

Strontium hydroxide is made by heating the carbonate in a current of superheated steam:

$$SrCO_3 + H_2O \rightarrow Sr(OH)_2 + CO_2.$$

This action takes place more easily than does the mere dissociation of the carbonate, because the formation of the hydroxide liberates energy, and this partially compensates for the energy which has to be provided to decompose the carbonate (*cf.* p. 78). The lowering of the partial pressure of the carbon dioxide by the steam also contributes to the result (*cf.* p. 595).

The hydrate crystallizes from water as $Sr(OH)_2,8H_2O$, and is employed in separating crystallizable sugar from molasses. By evaporation of the extract from the sugar-cane or beet-root, as much of the sugar as possible is first secured by crystallization. Then the molasses which remains is mixed with a saturated solution of strontium hydroxide. The resulting precipitate of sucrate of strontium, $C_{12}H_{22}O_{11}$, SrO, or $C_{12}H_{22}O_{11},2SrO$, is separated by a filter-press, made into a paste with water, and treated with carbon dioxide. A second filtration parts the insoluble carbonate of strontium from the solution of sugar, and the latter is evaporated and allowed to crystallize. Calcium hydroxide, which gives a tricalcium sucrate, is often employed in the same way.

Strontion is a bivalent ion, and gives insoluble compounds with carbonanion, sulphanion, and oxalanion. The presence of strontium is recognized by the carmine-red color which its compounds give to the Bunsen flame (see also below). Its spectrum shows several red bands and a very characteristic blue line.

Barium.

The physical and chemical properties of the compounds of barium recall those of strontium and calcium. All the compounds of barium which are soluble in water, or can be brought into solution by the weak acids of the digestive fluids, are poisonous.

Occurrence. — Like strontium, barium is found in the form of the carbonate, witherite $BaCO_3$, which is rhombic and isomorphous with

aragonite, and the sulphate $BaSO_4$, heavy-spar or barite (Gk. βαρύς, heavy), which is rhombic and isomorphous with anhydrite. The specific gravity of the sulphate is 4.5, while the specific gravity of other compounds of the light metals does not generally exceed 2.5. The free metal, which is silver-white, may be obtained by electrolysis of the molten chloride.

The compounds are made by treating the natural carbonate with acids directly, or by first reducing the sulphate with carbon to sulphide, or converting the carbonate into oxide, and then treating the products with acids.

Barium Carbonate. — This carbonate demands so high a temperature (about 1500°) for the attainment of a sufficient dissociation tension, and is so apt then to be partially protected from decomposition by the melting of the oxide, that special means is employed for its decomposition. It is heated with powdered charcoal (*cf.* p. 485):

$$BaCO_3 + C \rightarrow BaO + 2CO.$$

The precipitated form of the carbonate is made by adding sodium carbonate to the aqueous extract from crude barium sulphide (*q.v.*). The compound is also obtained by fusing pulverized barite with excess of sodium carbonate, and dissolving the sodium salts out of the residue.

The Sulphate and Sulphide. — The natural **sulphate** is the source of many of the compounds of barium. The precipitated sulphate, made by adding sulphuric acid to the aqueous extract from barium sulphide, is used in making white paint, in filling paper for glazed cards, and sometimes as an adulterant of white lead. The salt is highly insoluble in water and is hardly at all affected by aqueous solutions of chemical agents. It is somewhat soluble in hot, concentrated sulphuric acid, and the solution yields crystals of a compound $BaSO_4, H_2SO_4$, or $Ba(HSO_4)_2$. Calcium and strontium sulphates behave in the same way. All three compounds are decomposed by water, and give the insoluble sulphates.

Barium sulphide, like the sulphides of calcium and strontium (p. 604), is slightly soluble in water, but slowly passes into solution owing to hydrolysis and formation of the hydroxide and hydrosulphide. It is made by heating the pulverized sulphate with charcoal:

$$BaSO_4 + 4C \rightarrow BaS + 4CO.$$

The Chloride and Chlorate. — Barium chloride is generally manufactured by heating the sulphide with calcium chloride. The whole treatment of the heavy-spar is carried out in one operation:

$$BaSO_4 + 4C + CaCl_2 \rightarrow 4CO + BaCl_2 + CaS.$$

By rapid treatment with water, the chloride can be separated from the calcium sulphide before much decomposition of the latter (*cf.* p. 604) has taken place. Barium chloride crystallizes in rhombic tables as a dihydrate $BaCl_2, 2H_2O$. Aside from the difference in composition, this compound differs from the ordinary hydrated chlorides of calcium and strontium in being non-hygroscopic and in being capable of dehydration by heat without the formation of any hydrogen chloride (*cf.* p. 535).

Barium chlorate is made by treating the precipitated barium carbonate with a solution of chloric acid. It is deposited in beautiful monoclinic crystals, and is used with sulphur and charcoal in the preparation of "green fire."

The Oxides and Hydroxide. — The oxide of barium is manufactured from the carbonate or sulphide. In the latter case, moist carbon dioxide is passed over the sulphide, and the resulting carbonate is then treated with steam. The compound may be obtained in pure form by heating the nitrate. The oxide unites vigorously with water to form the hydroxide. When heated in a stream of air or oxygen it gives the dioxide BaO_2. This change and its reversal constitute the basis of Brin's process for obtaining oxygen from the air (p. 63). To protect the oxide from conversion into the carbonate and hydrate, which are not decomposable at the temperature employed, the air must be carefully purified from carbon dioxide and moisture.

Barium dioxide, when made by union of oxygen with the monoxide, is a compact gray mass. A hydrated form is thrown down as a crystalline precipitate when hydrogen peroxide solution is added to a solution of barium hydroxide:

$$Ba(OH)_2 + H_2O_2 \leftrightarrows BaO_2\downarrow + 2H_2O.$$

The crystals have the formula $BaO_2, 8H_2O$. Similar hydrates of the dioxides of strontium and calcium may be made in the same way. In all three cases the pure dioxides are obtained as white powders by removal of the water of hydration by very gentle heating *in vacuo* (*cf.* p. 276). The dioxides of strontium and calcium are not formed by direct union of oxygen with the oxides. Barium dioxide is used in the manufacture of hydrogen peroxide (p. 303).

Barium hydroxide is the most soluble of the hydroxides of this group, and gives, therefore, the highest concentration of hydroxidion. The solution is known as "baryta-water." It is also the most stable of the three hydroxides, and may be melted without decomposition. It crystallizes when a warm, saturated solution cools in the form $Ba(OH)_2, 8H_2O$. It is much used in quantitative analysis for making standard alkali-solutions. Solutions of sodium or potassium hydroxide may acquire varying proportions of carbonate by the action of carbon dioxide from the air, and their action on indicators loses thereby in sharpness. With barium hydroxide this is impossible, for the carbonate is insoluble, and is precipitated from the solution.

Barium Nitrate. — This salt is made by the action of nitric acid on the sulphide, oxide, hydroxide, or carbonate of barium. It crystallizes from aqueous solution without water of hydration.

Analytical Reactions of the Calcium Family. — Barion is a colorless, bivalent ion. Many of its compounds are insoluble in water, and the sulphate is insoluble in acids also. The spectrum given by the salts contains a number of green and orange lines.

In solutions of salts of calcium, strontium, and barium, the ions calcion, strontion, and barion may be distinguished by the fact that calcium sulphate solution will precipitate the strontium and barium as sulphates, but will leave salts of calcium unaffected. Similarly, strontium sulphate solution precipitates barium sulphate, and does not give any result with salts of the two first. The oxalate of calcium is precipitated in presence of acetic acid, while the oxalates of strontium and barium are not (*cf.* p. 599), and there are other differences of a like nature in the solubilities of the salts.

Exercises. — 1. Arrange the chromates of the metals of this family in the order of solubility (p. 544). Compare the solubilities with those of the carbonates, oxalates, and sulphates of the metals of the same family.

2. What must be the approximate total molar concentration of the solution of calcium chloride freezing at $-48°$ (p. 291)?

3. What is meant by fluorescence (*cf.* any book on physics)?

4. What will be the ratio by volume, at 150°, of the nitrogen peroxide and oxygen given off by the decomposition of calcium nitrate?

What would be the nature of the difference between the ratio at 150° and that at room temperature?

5. What fact about the heat of solution of gypsum is indicated by its change of solubility with temperature (p. 260)?

6. What is the significance of the fact that hydrated barium chloride gives no hydrogen chloride when heated?

7. What are the advantages of removing water of hydration *in vacuo* (p. 611)?

8. Explain in terms of the ionic hypothesis the precipitation of the sulphate of strontium by calcium sulphate solution, and the absence of precipitation when the latter is added to the solution of a soluble salt of calcium.

9. Construct a table for the purpose of comparing the properties of the free elements of this family and also the properties of their corresponding compounds.

10. Are the elements of this family typical metals? If not, in what respects do they fall short (p. 533)?

11. What inference do you draw from the fact that the oxalates of barium and strontium are not precipitated in presence of acetic acid, while the oxalate of calcium is so precipitated? Is the inference confirmed by reference to the data?

CHAPTER XXXVI

COPPER, SILVER, GOLD

THE three metals of this family, being found free in nature, are amongst those which were known in early times. They are the metals universally used for coinage and for ornamental purposes. They are the three best conductors of electricity (p. 533), and each represents the maximum of conductivity in the periodic series to which it belongs. In malleability and ductility silver is intermediate between gold and copper (p. 531), but in electrical conductivity it exceeds both.

The Chemical Relations of the Copper Family. — Copper (Cu, at. wt. 63.6), silver (Ag, at. wt. 107.93), and gold (Au, at. wt. 197.2), occupy the right side in the second column of the table of the periodic system (p. 411), and the chemical relations (p. 226) of these elements are in many ways in sharp contrast to those of the alkali metals, their neighbors, on the left side:

ALKALI METALS.	COPPER, SILVER, GOLD.
All univalent and give but one series of compounds. Halides all soluble in water.	Cu^I and Cu^{II}: two series. Ag^I: one series. Au^I and Au^{III}: two series. Halides of univalent series insoluble.
Very active; rapidly oxidized by air; displace all other metals from combination (E. M. series, p. 362).	Amongst least active metals; only copper is oxidized by air; displaced by most other metals. Hence, found free in nature (p. 362).
Oxides and hydroxides strongly basic, and halides not hydrolyzed (p. 534).	Oxides and hydroxides feebly basic (except Ag_2O); halides hydrolyzed (except Ag-halides). Hence, basic salts are numerous.
Never found in anion. Give no complex cations.	Frequently in anion, *e.g.*, $K.Cu(CN)_2$, $K.Ag(CN)_2$, $K.AuO_2$, $K.Au(CN)_2$, and in complex cation, *e.g.*, $Ag(NH_3)_2.OH$ and $Cu(NH_3)_4.(OH)_2$.

On account of their inactivity towards oxygen, and their easy recovery from combination by means of heat, silver and gold, together with the platinum family, are known as the "noble metals."

Univalent copper and gold resemble in some ways Hg^I and Tl^I,

while bivalent copper resembles Zn^{II}, Mn^{II}, Fe^{II}, and Ni^{II}, and trivalent gold resembles Al^{III} and Fe^{III}. This family is, in fact, not homogeneous, and the close relation which, amongst metals, subsists between valence and chemical properties makes comparisons with elements of entirely different families often the most suggestive.

Copper.

Chemical Relations of the Element. — Copper is the first metallic element showing two valences which we have encountered. In such cases two more or less complete, independent series of salts are known. These are here distinguished as cuprous (univalent) and cupric (bivalent) salts. The methods by which a compound of one series may be converted into the corresponding compound of the other series should be noted.

The chief cuprous compounds are Cu_2O, CuCl, CuBr, CuI, CuCN, Cu_2S. There are no cuprous salts of oxygen acids. The cuprous compound is in each case more stable (p. 119) than the corresponding cupric compound, and is formed from it either by spontaneous decomposition, as in the cases of the iodide and cyanide ($2CuI_2 \rightarrow 2CuI + I_2$), or on heating. The cuprous halides and cyanide are colorless and insoluble in water; but the chloride, being easily oxidized by air to the cupric condition, quickly turns green. The ion $Cu^{\cdot}$ (monocuprion) seems to be colorless.

The cupric compounds are more numerous, as they include also salts of oxygen acids, like $CuSO_4$, $Cu(NO_3)_2$, etc. CuI_2 and $Cu(CN)_2$ cannot be obtained in pure form, as they decompose, giving the cuprous salts. The anhydrous salts are usually colorless or yellow, but the ion $Cu^{\cdot\cdot}$ (dicuprion) is blue, and so, therefore, are the aqueous solutions of the salts. The cupric are more familiar than the cuprous compounds, since cupric oxide, sulphate, and acetate are the compounds of copper which most frequently find employment in chemistry and in the arts. All the soluble salts of copper are poisonous.

In electrolyzing salts of copper, a given amount of electricity will deposit twice as much copper from a cuprous salt as from a cupric salt (p. 316), since monocuprion carries only half as great a charge, weight for weight, as dicuprion.

Writers on chemistry frequently double (Cu_2Cl_2, etc.) the formulæ of cuprous salts. The molecular weights in organic solvents (*cf.* p. 292), however, in many cases accord with the simple formulæ. Some higher

molecular weights observed in solution and the vapor density of cuprous chloride (6.6, corresponding nearly to Cu_2Cl_2) might be regarded as being due to association (imperfect dissociation, *cf.* p. 205). The formation of numerous double or complex compounds like HCl,CuCl (= $HCuCl_2$), which may be regarded as acid salts, however, lends support to the view that the formulæ should be doubled. Inasmuch as the behavior of the salts is sufficiently well represented by the simple formulæ, these are here used throughout (see under Silver, p. 626).

Occurrence. — Copper is found free in the Lake Superior region, in China, and in Japan. The sulphides, copper pyrites $CuFeS_2$ and chalcocite Cu_2S, are worked in Montana, in southwest England, in Spain, and in Germany. Malachite, $Cu_2(OH)_2CO_3$ (= $Cu(OH)_2,CuCO_3$), and azurite, $Cu_3(OH)_2(CO_3)_2$ (= $Cu(OH)_2,2CuCO_3$), both basic carbonates, are mined in Siberia and elsewhere. Cuprite or ruby copper Cu_2O is also an important ore. The name of the element comes from the fact that in ancient times copper mines, long since worked out, existed in Cyprus. The element is found in the feathers of some birds, in the hæmocyanin of the blood of the cuttle-fish, which is blue when arterial and colorless when venous, and elsewhere in living organisms.

Extraction from Ores. — For isolating native copper it is only necessary to separate the metal, by grinding and washing, from the rock through which it ramifies, and to melt the almost pure powder of copper with a flux (p. 540). The carbonate and oxide ores require coal, in addition, for the removal of the oxygen.

The liberation of copper from the sulphide ores is difficult, and often involves very elaborate schemes of treatment. This arises from two causes. Other metals, such as iron and zinc, unite with oxygen more readily than with sulphur, and hence the sulphides are easily converted into oxides by roasting with free access of air; with copper it is just the reverse. Thus, even great excess of air and repeated roasting produce only a gradual diminution in the amount of sulphur in the mass. Then, many copper ores contain a large amount of the sulphides of iron, and these have to be removed by conversion into oxide (by roasting) and then into silicate (with sand). The silicate forms a flux, and separates itself from the molten mixture of copper and copper sulphide ("matte"). In Montana it is found possible to abbreviate the treatment. The ore is first roasted until partially oxidized. It is then melted in a cupola or a reverberating furnace, and placed in large iron

vessels like Bessemer converters (*q.v.*) provided with a lining rich in silica. A blast of air mixed with sand is now blown through the mass. The iron is completely oxidized to FeO and made into silicate, the sulphur escapes as sulphur dioxide, and arsenic and lead are likewise removed by this treatment. The silicate of iron floats as a slag upon the copper when the contents of the converter are poured out. The resulting copper is pure enough to be cast in large plates and purified by electrolysis (see below).

Wet processes are used for poor ores. In one of these the ore is roasted with salt. The copper is thus converted into cupric chloride, and can be dissolved away from the oxide of iron and other materials by means of water. Any traces of silver which may have been present pass also into solution (as AgCl), and are precipitated by addition of potassium iodide. The copper is then displaced by means of scrap iron, and forms a brown sludge ($Cu^{\cdot\cdot} + Fe\uparrow \rightarrow Fe^{\cdot\cdot} + Cu\downarrow$).

The properties of copper are seriously affected by small amounts of impurities, such as cuprous oxide or sulphide, which are soluble in the molten metal. Then, too, the difficulties in the way of its preparation are aggravated by the high standard of purity demanded in order that it may have the maximum tenacity, ductility, and conductivity which its various applications require. Hence a large proportion of the copper on the market is purified by electrolysis, a method which meets the case by giving a copper in which foreign materials can be shown to be present only by the most refined tests. In this method of refining the metal, thin sheets of copper, coated with graphite to permit easy removal of the deposit, form the cathodes, and thick plates of copper the anodes. These are suspended alternately and close together in large troughs filled with cupric sulphate solution. The cathodes are all connected with the negative wire of the dynamo, and the anodes with the positive one. The $Cu^{\cdot\cdot}$ is attracted to the cathodes and is deposited upon them. The SO_4'' migrates towards the anodes, where copper from the thick plate becomes ionized in equivalent amount. The stock of cupric sulphate thus remains the same, and the practical effect of the electrolysis is to carry copper across from one plate to the other (*cf.* p. 325). The cathodes are removed from time to time, and the deposit of copper is stripped from their surface. Fresh anodes are substituted when the old ones are eaten away. Since there is no polarization, a current of less than 0.5 volt suffices. The copper is deposited in pure form, although an impure anode is employed, because metals like gold, silver, and antimony, which succeed copper in the electro-

motive series (p. 362), and compounds like cuprous sulphide, do not become ionized. They fall to the bottom of the tank as a fine powder. Similarly, metals like zinc, which displace copper, although they are dissolved, are not again deposited. This will be understood when it is considered that, if they were to be deposited, they would displace copper from the solution and dissolve. Since the copper, as deposited on the cathodes, is crystalline and porous, it is afterwards melted and cast into blocks or bars.

In 1900 the United States produced 60 per cent of the world's copper, Great Britain 16 per cent, and Germany 6 per cent. The proportions of the whole consumed in each of these countries were 33, 22, and 22 per cent, respectively.

Physical Properties.—Copper is red by reflected and greenish by transmitted light. Native copper shows crystals of the regular system (p. 530). It melts at 1057°, and therefore much more easily than pure iron (1800°). When steel draw-plates are used it can be drawn into wire with a diameter of only 2 mm., and by means of plates provided with perforated diamonds the diameter of the wire can be reduced to .03 mm. (1 kilometer weighs only 7 g.). The metal after drawing is more tenacious but conducts electricity less well.

Chemical Properties.—In dry oxygen, copper does not rust. In moist oxygen a thin film of cuprous oxide is formed, and in ordinary air a green basic carbonate (*not* verdigris, *q.v.*). It does not decompose water at any temperature or displace hydrogen from dilute acids (p. 362). On the other hand, hydrogen, absorbed in platinum or even in charcoal, liberates copper ($Cu^{\cdot\cdot} + H_2 \rightarrow Cu + 2H^{\cdot}$) when immersed in solutions of copper salts. The metal attacks oxygen acids (pp. 379, 446), however. Again, acids like hydrochloric acid, in conjunction with oxygen from the air, do act slowly upon copper ($2Cu + 4HCl + O_2 \rightarrow 2CuCl_2 + 2H_2O$). This sort of simultaneous action of two agents is frequently used, as in making silicon tetrachloride (p. 520). In a similar way sea-water and air slowly corrode the copper sheathings of ships, giving a basic chloride, $Cu_4(OH)_6Cl_2, H_2O (= 3Cu(OH)_2, CuCl_2, H_2O)$, which is found in nature as atakamite.

On account of its resistance to the action of acids, copper is used for many kinds of vessels, for covering roofs and ships' bottoms, and for coins. It furnishes also electrotype reproductions of medals, of engraved plates, of type, etc. For this purpose a cast of the object

is first made in gutta percha, plaster of paris, or wax. This is then coated with graphite to give it a conducting surface, and receives an electrolytic deposit of copper. Great quantities of the metal are used in electrical plants and appliances.

Alloys. — The qualities of copper are modified for special purposes by alloying it with other metals. **Brass** contains 18–40 per cent of zinc, and melts at a lower temperature (p. 532) than does copper. A variety with little zinc is beaten into thin sheets, giving Dutch-metal ("gold-leaf"). **Bronze** contains 3–8 per cent of tin, 11 or more per cent of zinc, and some lead. It was used for making weapons and tools before means of hardening iron were known, and later, on account of its fusibility, continued to be employed for castings until displaced largely by cast-iron (discovered in the eighteenth century). For works of art it is preferred to copper because of its fusibility, its color, and its more rapid acquirement of a much prized "patina" due to surface corrosion. Artificial "bronzing" of brass is effected by applying a solution of arsenious oxide in hydrochloric acid ($AsCl_3$). The zinc displaces some arsenic, which combines with the copper. Brass instruments are "bronzed" by means of a dilute solution of chloroplatinic acid (*q.v.*), from which the zinc displaces platinum. **Gun-metal** contains 10 per cent, and **bell-metal** 25 per cent of tin. **German silver** contains 19–44 per cent of zinc and 6–22 per cent of nickel, and shows none of the color of copper. **Aluminium-bronze** contains 5–10 per cent of aluminium, and resembles gold in color. When it contains some iron it can be worked at a red heat, but not welded. **Silicon-bronze** contains not more than 5 per cent of silicon, and is made by adding silicide of copper (made in the electric furnace, p. 457) to copper. It has usually only 60 per cent of the conductivity of pure copper, but is nearly twice as tenacious, and is used for telephone and over-head electric wires. **Phosphor-bronze** contains copper and tin (100 : 9) with $\frac{1}{2}$–1 part of phosphorus, and is employed for certain parts of machines. Ships' propellers are made of **manganese-bronze** (30 per cent manganese).

Cupric Chloride. — This compound is made by union of copper and chlorine, by treating the hydrate or carbonate with hydrochloric acid, or by heating copper with hydrochloric acid and some nitric acid, the latter being used simply as an oxidizing agent ($Cu + 2HCl + O \rightarrow CuCl_2 + H_2O$). The blue crystals of a hydrate, $CuCl_2,2H_2O$, are deposited by the solution. The anhydrous salt is yellow. Dilute solu-

tions are blue, the color of dicuprion, but concentrated solutions are green on account of the presence of the yellow molecules (p. 335). The aqueous solution is acid in reaction (p. 344). When excess of ammonium hydroxide is added to the solution, the basic chloride, cupric oxychloride $Cu_4(OH)_6Cl_2$ (p. 618), which is at first precipitated, redissolves, and a deep-blue solution is obtained. This on evaporation yields deep-blue crystals of hydrated ammonio-cupric chloride $Cu(NH_3)_4.Cl_2, H_2O$. The deep-blue color of the solution, which is given by all cupric salts, is that of the $Cu(NH_3)_4^{\cdot\cdot}$ ion. The dry salt also absorbs ammonia, giving $CuCl_2, 6NH_3$. This and the preceding compound have an appreciable tension of ammonia, and when warmed leave $CuCl_2, 2NH_3$. Reduction of pressure or rise of temperature results in the final loss of all the ammonia (*cf.* p. 122).

Cuprous Chloride. — This salt is formed when cupric chloride is heated ($2CuCl_2 \rightleftarrows 2CuCl + Cl_2$). It may be made by adding hydrochloric acid to cupric chloride solution, and boiling the mixture with copper turnings:

$$CuCl_2 + Cu \rightarrow 2CuCl \text{ or } Cu^{\cdot\cdot} + Cu \rightarrow 2Cu^{\cdot}.$$

The solution contains compounds of cuprous chloride with hydrogen chloride $HCl, CuCl$ or $HCuCl_2$ and H_2CuCl_3, which are decomposed when water is added. The cuprous chloride is insoluble in water, and forms a white crystalline precipitate.

Cuprous chloride is hydrolyzed quickly by hot water, giving, finally, red, hydrated cuprous oxide, Cu_2O. When dry it is not affected by light, but in the moist state becomes violet and, finally, nearly black. The action is said to be $2CuCl \rightarrow CuCl_2 + Cu$. In moist air it turns green, and is oxidized to cupric oxychloride (p. 618). It is dissolved by hydrochloric acid, giving the colorless complex acids $HCuCl_2$ and H_2CuCl_3. The solution is oxidized by the air, turning first brown and then green, and finally depositing the cupric oxychloride. Cuprous chloride also dissolves in ammonium hydroxide, giving $Cu(NH_3)_2.Cl$, the ion $Cu(NH_3)_2^{\cdot}$ being colorless. The solution is quickly oxidized by the air, turns deep-blue, and then contains $Cu(NH_3)_4^{\cdot\cdot}$. The solution of cuprous chloride in hydrochloric acid is used for absorbing carbon monoxide from gaseous mixtures. A crystalline compound ($CuCl, CO, 2H_2O$?) has been isolated from the solution.

The Bromides and Iodides of Copper. — By treatment of cupric oxide with hydrobromic acid and slow evaporation of the solution, jet-black crystals of anhydrous cupric bromide ($CuBr_2$) are obtained. A concentrated aqueous solution is deep-brown in color, and the gradual ionization of the molecules as the solution is diluted is well shown by this salt (p. 335). The ionization is here accompanied by evolution of heat (p. 330), as it is also in the cases of cupric chloride and cupric sulphate, and in the ionized condition the substances contain less available energy than in the molecular. In these cases, therefore, when the temperature is raised the ionization diminishes (p. 260). It will be remembered that ordinary thermal dissociation invariably increases with rise in temperature, and is always accompanied by absorption of heat. Ionic dissociation, however, may be either endothermal or exothermal.

When cupric bromide is heated, bromine is given off, and **cuprous bromide** CuBr remains.

Cupric iodide appears to be unstable at ordinary temperatures. When a soluble iodide is added to a cupric salt, a white precipitate of **cuprous iodide** and free iodine are obtained:

$$2Cu^{\cdot\cdot} + 4I' \leftrightarrows 2CuI\downarrow + I_2.$$

The iodine may be dissolved in excess of the soluble iodide (p. 235), or reduced to hydrogen iodide with sulphurous acid (p. 394).

The Solution of Insoluble Salts when Complex Ions are Formed. — The solution of an insoluble salt like cuprous chloride by hydrochloric acid or ammonium hydroxide is typical of a great variety of actions of which we here meet one of the first examples (*cf.* p. 363).

Since a salt is normally less soluble in an acid having the same anion (p. 581), the dissolving of cuprous chloride in hydrochloric acid requires a special explanation, namely, the fact that here two complex acids $H.CuCl_2$ and $H_2.CuCl_3$ are formed. The chloridion of the hydrogen chloride must indeed tend to repress the ionization of the dissolved part of the cuprous chloride, so that a smaller concentration of $Cu^{\cdot}$ remains. But the complex negative ion $CuCl_2'$ (or $CuCl_3''$) which is formed, is very little dissociated, and gives a still smaller concentration of $Cu^{\cdot}$ ($CuCl_2' \rightleftarrows Cu^{\cdot} + 2Cl'$). Thus this complex ion is formed at the expense of the $Cu^{\cdot}$ of the insoluble cuprous chloride, and the latter goes into solution progressively in the effort to restore the balance:

$$\begin{array}{llll} CuCl\,(solid) \leftrightarrows & CuCl\,(diss'd) \rightleftarrows & Cl' + Cu^{\cdot} & \multirow{2}{*}{$\Big\} \rightleftarrows CuCl_2'.$} \\ & 2HCl \rightleftarrows & 2H^{\cdot} + 2Cl' & \end{array}$$

The same exact laws of equilibrium used in discussing the dissolving of salts by acids with a different anion (p. 599) may be applied to the whole procedure.

Similar behavior is shown by the cyanides of copper, silver, iron, etc. (*q.v.*), of which many complex compounds are known.

The dissolving of cuprous chloride by the free ammonia of ammonium hydroxide is explained in the same way. The only difference is that here the copper is in the complex positive ion. The ion $Cu(NH_3)_2^{\cdot}$ gives little $Cu^{\cdot}$ — less than does cuprous chloride, in spite of the insolubility of the latter. Hence the salt passes into solution until the ion-product $[Cu^{\cdot}] \times [Cl']$, with continually increasing $[Cl']$, reaches its normal value or until the solid is exhausted.

The deep-blue colored ion $Cu(NH_3)_4^{\cdot\cdot}$ given by cupric chloride and other cupric salts is also very little ionized. Hence ammonium hydroxide dissolves all the insoluble cupric compounds save only cupric sulphide, which is the most insoluble of all — that is, the one giving the smallest concentration of dicuprion. Conversely, the sulphide is the only insoluble compound of copper which can be precipitated from ammoniacal solution. Zinc and other more active metals, however, slowly precipitate metallic copper, thereby showing that some dicuprion is present.

Cuprous Oxide. — This oxide is red in color, and natural specimens show octahedral forms. It is produced by oxidation of finely divided copper at a gentle heat, or by the addition of bases to cuprous chloride, and is best made by the action of glucose on cupric hydroxide. The latter is reduced by the former, and the resulting hydrated cuprous oxide forms a pale-brown precipitate which quickly becomes bright red. The simple hydrate, CuOH, is unknown, but the above mentioned precipitate has approximately the composition $4Cu_2O,H_2O$, and yields Cu_2O when heated.

Cuprous oxide is acted upon by hydrochloric acid, giving cuprous chloride, or rather $HCuCl_2$. It also dissolves in ammonium hydroxide, giving, probably, $Cu(NH_3)_2.OH$, which is colorless. With dilute oxygen acids part of it is oxidized, giving the cupric salt, and part is reduced to metallic copper:

$$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + H_2O.$$

Cupric Oxide and Hydroxide. — Cupric oxide is a black substance formed by heating copper in a stream of oxygen or by igniting

the nitrate, carbonate, or hydroxide. It absorbs moisture from the air, although it is not soluble in water. When heated strongly it loses some oxygen, and is partly reduced to cuprous oxide. Its chief use is in the **analysis of compounds of carbon**. When heated with the latter, it oxidizes the hydrogen to water, and the carbon to carbon dioxide. The operation is performed in a tube through which passes a stream of oxygen, and the products are caught in glass vessels containing calcium chloride and potassium hydroxide, respectively.

Cupric hydroxide is precipitated as a gelatinous substance by addition of sodium or potassium hydroxide to a solution of a cupric salt ($Cu^{\bullet\bullet} + 2OH' \rightarrow Cu(OH)_2$). When the mixture is boiled, the hydroxide loses water and forms a black hydrated cupric oxide ($Cu(OH)_2, 2CuO$?). The hydroxide is soluble in ammonium hydroxide, with formation of the compound $Cu(NH_3)_4^{\bullet\bullet}(OH)_2$, which imparts a deep-blue color to the solution. Various forms of cellulose, such as filter paper and cotton, dissolve in this solution, and are reprecipitated when the ammonium hydroxide is neutralized with acids. Cupric hydroxide dissolves also in a solution of sodium tartrate ($Na_2.C_4H_2O_4(OH)_2$), giving a deep-blue liquid (practically "Fehling's solution"). In this action, it enters into the negative ion, as is shown by electrolysis, interacting apparently with the hydroxyl groups of the tartranion. In this condition it is reduced by sugars (see above) with especial ease, and is in this form used as a test for them.

Cupric Nitrate. — The nitrate is made by treating cupric oxide or copper with nitric acid (p. 446), and is obtained from the solution as a deliquescent, crystalline hydrate. The hexahydrate is secured at temperatures below 24.5°, its transition point (p. 594), and the trihydrate from 24.5° up to 114.5° (its transition point; see under Manganous sulphate). When dehydrated at 65° the salt is partly hydrolyzed, and a basic nitrate $Cu_4(OH)_6(NO_3)_2$ remains.

Carbonate of Copper. — No normal carbonate ($CuCO_3$) can be obtained. A basic carbonate (malachite) is found in nature, and is precipitated by adding soluble carbonates to cupric salts:

$$2CuSO_4 + 2Na_2CO_3 + H_2O \rightarrow Cu_2(OH)_2CO_3 + 2Na_2SO_4 + CO_2.$$

Presumably, the carbonate, if formed, would be hydrolyzed by water.

Cyanides of Copper. — When potassium cyanide is added to a solution of a cupric salt, cupric cyanide is precipitated. This is not stable, however, and gives off cyanogen, leaving cuprous cyanide:

$$2Cu(CN)_2 \rightarrow 2CuCN + C_2N_2.$$

Cuprous cyanide is insoluble in water, but interacts with an excess of potassium cyanide solution, producing a colorless liquid, from which $KCN,CuCN$, or $K.Cu(CN)_2$, potassium cuprocyanide, may be obtained in colorless crystals. The complex anion $Cu(CN)_2'$ is so little ionized to $Cu^{\cdot}$ and $2CN'$ that all insoluble copper compounds, *including cupric sulphide*, are dissolved by potassium cyanide; and none of them can be precipitated from the solution. Zinc is actually unable to displace copper from such a solution. The cause of the solution of the salts is the same as when the complex ions $Cu(NH_3)_2^{\cdot}$, $Cu(NH_3)_4^{\cdot\cdot}$, and $CuCl_2'$ are formed (p. 621).

Cupric Acetate. — By the oxidation of plates of copper, separated by cloths saturated with acetic acid (vinegar), a basic acetate of copper (**verdigris**) is obtained:

$$6Cu + 8HC_2H_3O_2 + 3O_2 \rightarrow 2Cu_3(OH)_2(C_2H_3O_2)_4 + 2H_2O.$$

It is used in manufacturing green paint, is insoluble in water, and is unaffected by light. It dissolves in acetic acid, and green crystals of the normal acetate $Cu(C_2H_3O_2)_2,H_2O$ are obtained from the solution. The basic acetate is used in preparing **paris green**. A hot solution of arsenious acid (H_3AsO_3) is mixed with a paste of verdigris and a little acetic acid and boiled. A precipitate of paris green $Cu(C_2H_3O_2)_2,Cu_3As_2O_6$, which has a unique light-green color, is thrown down. On account of their poisonous nature, this compound and **Scheele's green** ($CuHAsO_3$) are little used as pigments. The former is chiefly made for use in the extermination of potato-beetles and other insects and employment in the destruction of parasitic fungi.

Cupric Sulphate. — This salt is obtained by heating copper in a furnace with sulphur, and admitting air to oxidize the cuprous sulphide. The mixture of cupric sulphate and cupric oxide which is formed is treated with sulphuric acid. The salt is also made by allowing dilute sulphuric acid to trickle over granulated copper while air has free access to the material ($2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 +$

$2H_2O$). When concentrated and at a high temperature, sulphuric acid will itself act as the oxidizing agent (*cf.* p. 379).

Cupric sulphate crystallizes as pentahydrate $CuSO_4, 5H_2O$ in blue asymmetric crystals (Fig. 41, p. 120), and in this form is called blue-stone or blue vitriol. The dissociation of this hydrate has been discussed on page 122. The aqueous solution has an acid reaction (p. 344). The anhydrous salt is white, and can be crystallized in thin needles (rhombic system ?) from solution in hot, concentrated sulphuric acid (*cf.* pp. 120–123). Cupric sulphate is employed for making other compounds of copper, in copper-plating (p. 618), in batteries, as a mordant in dyeing (*q.v.*) and calico-printing, and, as a germicide and insecticide, for spraying plants.

When ammonium hydroxide is added to cupric sulphate solution, a pale-green basic salt ($Cu_4(OH)_6SO_4$?) is first precipitated. With excess of the hydroxide the blue $Cu(NH_3)_4^{\cdot\cdot}$ ion (p. 620) is formed, and crystals of ammonio-cupric sulphate $Cu(NH_3)_4.SO_4, H_2O$ can be obtained from the solution. This compound easily loses water and ammonia (by stages), leaving successively $CuSO_4, 2NH_3$ and $CuSO_4, NH_3$. Cupric sulphate also combines with potassium and ammonium sulphates, giving double salts of the form $CuSO_4, K_2SO_4, 6H_2O$, which are deposited in large, monosymmetric crystals from the mixed solutions (see Zinc sulphate).

The Sulphides of Copper. — Cuprous sulphide Cu_2S occurs in nature in rhombic crystals of a gray, metallic appearance. It is made by heating cupric sulphide, a stream of hydrogen gas being used to assist the removal of the excess of sulphur.

Cupric sulphide is deposited as a black precipitate when hydrogen sulphide is led through a solution of a cupric salt. Made in this way, it is always partly decomposed into $Cu_2S + S$. By cautiously treating copper with excess of sulphur at 114° it may be obtained as a blue crystalline solid. At higher temperatures it gives off sulphur.

Analytical Reactions of Compounds of Copper. — The ion of ordinary cupric salts, dicuprion $Cu^{\cdot\cdot}$, is blue, and that of cuprous salts, monocuprion $Cu^{\cdot}$, is colorless. Cuprous solutions, however, are easily oxidized by the air and become blue. In solutions containing dicuprion, hydrogen sulphide precipitates cupric sulphide, even in presence of acids (p. 600). Bases throw down the blue hydroxide, and carbonates precipitate a green basic salt (p. 623). Potassium fer-

rocyanide gives the brown, gelatinous cupric ferrocyanide ($2Cu.SO_4 + K_4.Fe(CN)_6 \rightleftarrows Cu_2.Fe(CN)_6\downarrow + 2K_2SO_4$). A very characteristic test is the formation of the deep-blue $Cu(NH_3)_4^{\cdot\cdot}$ ion with excess of ammonium hydroxide. This solution itself gives a precipitate with hydrogen sulphide only. Solutions of complex cuprous and cupric cyanides such as $K.Cu(CN)_2$ and $K_2.Cu(CN)_4$ are colorless, and do not respond to any of the above tests. With microcosmic salt or borax (pp. 468, 528), copper compounds form a bead which is green in the oxidizing part of the flame and becomes red and opaque (liberation of copper) in the reducing flame.

SILVER.

Chemical Relations of the Element. — This element presents a curious assortment of chemical properties. It differs from copper in having a strongly basic oxide, in giving salts with active acids which are not hydrolyzed by water, and in forming neutral rather than basic salts. In these respects it approaches the metals of the alkalies and alkaline earths. It resembles copper in entering into complex compounds, and in giving insoluble halides like the cuprous halides. It differs from both copper and the metals of the alkalies, and resembles gold and platinum, in that its oxide is easily decomposed by heat, with formation of the free metal, and in the low position it occupies in the electromotive series and the consequent slight chemical activity of the free metal.

The salts are always represented by the simplest formula, AgCl, etc., although in organic solvents greater tendencies to polymerization are observed than in the case of the cuprous compounds (p. 615).

Occurrence. — Native silver, sometimes found in large masses, although more usually scattered through a rocky matrix, contains varying amounts of gold and copper. Native copper always contains dissolved silver. Sulphide of silver (Ag_2S) occurs alone and dissolved in galenite (PbS), with which it is isomorphous. Smaller amounts of the metal are obtained from pyrargyrite Ag_3SbS_3 and proustite Ag_3AsS_3, which are silver sulphantimonite and sulpharsenite respectively, and from horn-silver AgCl.

Metallurgy. —The silver contained free, or as sulphide, in ores of copper and lead, is found in the free state dissolved in the metals extracted from these ores, and is secured by refining them. In the electrolytic refining of copper, silver is obtained from the mud deposited in

the baths (p. 617). The proportion present in lead is usually small. Formerly the **Pattinson desilverizing process** was largely employed. In it the metallic lead is melted in iron vessels, and the crystals of lead, deposited as the metal slowly loses heat, are raked out. These consist at first of pure lead (*cf.* p. 294). When the remaining liquid becomes saturated with silver it begins to deposit lead and silver together. At this point the residue is placed in a hollow, lined with bone-ash, forming part of a reverberatory furnace (Fig. 100, p. 572), and heated strongly while a blast of air passes over its surface. In this process, called "cupellation," the lead is converted into litharge (PbO), which, driven by the air, flows in molten condition over the edge of the cupel. When the last trace of lead is gone, the shining surface of the pure silver "flashes" into view (*cf.* p. 547). **Parke's process,** which has superseded the above, takes advantage of the fact that molten zinc and lead are practically insoluble in one another, while silver is much more soluble in zinc than in lead. Lead dissolves 1.6 per cent of zinc, and zinc 1.2 per cent of lead. The principle is the same as in the removal of iodine from water by ether (p. 155). The lead is melted and thoroughly mixed by machinery with a small proportion of zinc. After a short time the zinc floats to the top, carrying with it in solution almost all of the silver, and solidifies at a temperature at which the lead is still molten. The zinc-silver alloy is skimmed off, and heated moderately in a furnace to permit the adhering lead to drain away. The zinc is finally distilled off in clay retorts, and the lead remaining with the silver is removed by cupellation.

Ores of silver which do not contain much or any lead are often smelted with lead ores, and the product is treated as described above, but many **other processes** are in use. Thus, sulphide ores are sometimes roasted until the iron and part of the copper are converted into oxide while the rest of the copper and all the silver remain as sulphate. The metal is secured by extracting the mass with water and precipitating the silver by means of copper (p. 362). Some ores are roasted with salt, and the resulting chloride of silver is dissolved out with sodium thiosulphate, or even strong brine. In Mexico the "patio" process has been in use since 1557. The sulphide is converted into chloride by the action of cupric chloride. Metallic mercury displaces the silver ($AgCl + Hg \rightarrow HgCl + Ag$), and, being present in excess, dissolves it. The treatment occupies several weeks, and much mercury is consumed. The amalgam is finally secured by "washing," and the mercury is separated from the silver by distillation.

In 1899 the production of silver in the United States was 2915 tons, in Mexico 1418 tons, in Europe 1138 tons. During the first half of the nineteenth century the total world's output averaged only 643 tons per year. Up to 1870 a gram of gold could buy 15.5 g. of silver. Now that the production has reached 6000 tons, the same amount of gold purchases about 35 g.

Physical Properties. — Pure silver is almost perfectly white. It melts at 960°. Its ductility is so great that wires can be drawn of such fineness that 2 kilometers of the finest wire weigh only about 1 g. In the molten condition it absorbs mechanically about twenty-two times its own volume of oxygen, but gives up almost all of this as it solidifies. Fantastically irregular masses result from the "sprouting" or "spitting" which accompanies the escape of the gas.

By addition of ferrous citrate to silver nitrate, a red solution and lilac precipitate of free silver can be made. The latter, after washing with ammonium nitrate solution, gives a red solution in water. Other solutions of colloidal (*cf.* p. 523) silver showing a variety of colors have been prepared by Cary Lea. Such colloidal solutions of metals are formed also by passing an electrical discharge between wires of silver, gold, or platinum held under water.

Silver is alloyed with copper to render it harder. The silver coinage of the United States and the continent of Europe has a "fineness of 900" (900 parts of silver in 1000), and that of Great Britain 925. Silver ornaments have a fineness of 800 or more. A superficial layer of almost pure-white silver is produced by heating the object in the air and dissolving out the cupric oxide thus formed with dilute sulphuric acid. The surface of the products, if not subsequently burnished, is "frosted." "Oxidized silver" is made by dipping objects made of the metal in a solution of potassium hydrogen sulphide, whereby a thin film of silver sulphide is produced.

Chemical Properties. — Silver does not combine with oxygen, either in the cold or when heated. It does not ordinarily displace hydrogen from aqueous solutions of acids, but its tendency to form the sulphide is so great that it decomposes hydrogen sulphide and alkali sulphides (*cf.* p. 391). It also displaces hydrogen when boiled with concentrated hydriodic acid, giving $AgI.HI$. Silver interacts with cold nitric acid and with hot, concentrated sulphuric acid, giving the nitrate or sulphate of silver and oxides of nitrogen or of sulphur (p. 446).

Since its hydroxide has no tendency to behave as an acid, alkalies, whether in solution or fused, have no action upon silver. Hence alkaline substances are heated in vessels of this metal or of iron, rather than in vessels of platinum (*q.v.*), because platinum is attacked by alkaline materials.

The Halides of Silver. — The chloride, bromide, and iodide are formed as curdy precipitates when a salt of silver is added to a solution containing the appropriate halide ion. The first is white, and melts at about 457°. The second and third are very pale-yellow and yellow respectively. The insolubility in water, which is very great, increases in the above order. The iodide, after melting, solidifies and forms quadratic crystals, which, as they cool, pass at 146° into a different physical variety (hexagonal) with evolution of heat (*cf.* pp. 368, 565).

When exposed to light, the chloride becomes first violet and finally brown, chlorine being liberated. The bromide and iodide behave similarly. It is believed that a sub-chloride and sub-bromide Ag_2Cl and Ag_2Br are formed in the early stages of the action (see Photography, below). Solid silver chloride absorbs ammonia, forming first $2AgCl, 3NH_3$, and then $AgCl,3NH_3$, the former with a tension of 93 mm., and the latter with a tension of about one atmosphere of ammonia at 20° (*cf.* p. 123). The bromide forms no compound in this way, but the iodide yields $2AgI,NH_3$.

In consequence of the progressive insolubility, a cold solution of a bromide will slowly convert the precipitate of silver chloride into bromide, and a soluble iodide will similarly transform the bromide or the chloride into iodide (*cf.* p. 585). Chlorine gas, however, displaces bromine and iodine from the dry compounds (*cf.* p. 361). This illustrates well the absence of any relation between the electromotive series and double decomposition (p. 362).

Silver fluoride may be made by treating the oxide or carbonate with hydrofluoric acid ($H_2F_2 + Ag_2O \rightarrow 2AgF + H_2O$). The salt is very soluble and deliquescent.

Complex Compounds of Silver. — Silver chloride dissolves easily in excess of ammonium hydroxide, giving the complex cation $Ag(NH_3)_2^{\cdot}$. Under certain conditions octahedral crystals (Fig. 48, p. 138) of AgCl are deposited from the solution, and, under other conditions, crystals of the composition $2AgCl, 3NH_3$. The bromide, which is less readily soluble,

gives the same complex ion. The iodide is hardly soluble at all. Ammonio-argention $Ag(NH_3)_2^{\cdot}$, in solutions of concentrations such as are commonly used (.1 N to N), gives about the same concentration of argention $Ag^{\cdot}$ as does the bromide, and much more than the highly insoluble iodide (*cf.* p. 544). Hence the latter is almost insoluble in ammonium hydroxide, and can be precipitated in ammoniacal solution. All three of the insoluble halides dissolve in solutions of potassium cyanide and of sodium thiosulphate, as do also all the other insoluble silver salts. Usually an equivalent amount of the cyanide or thiosulphate suffices, but for solution of the sulphide an excess is required. With the cyanide, double decomposition gives first the insoluble silver cyanide (AgCN) which then dissolves, forming the soluble potassium argenticyanide $K.Ag(CN)_2$. The thiosulphate gives a solution from which crystals of a complex salt $2NaAgS_2O_3, Na_2S_2O_3$ are obtained. The complex anion in the solution appears to be $Ag(S_2O_3)_2'''$. Since the iodide dissolves in the thiosulphate with considerable difficulty, we should infer that the complex thiosulphate anion gives about the same concentration of argention as does the iodide. An independent method of measuring the concentrations of argention in all the solutions, places the compounds in the order of diminishing ability to give argention thus, AgCl, $Ag(NH_3)_2^{\cdot}$, AgBr, $Ag(S_2O_3)_2'''$, AgI, $Ag(CN)_2'$, Ag_2S, and confirms the above inferences (see Concentration cells). The more active metals, like zinc and copper, displace silver from all solutions, whether the solutions contain simple or complex salts.

Oxides of Silver. — When sodium or potassium hydroxide is added to a solution of a salt of silver, a pale-brown precipitate is obtained, which, after being freed from water, is found to be Ag_2O. We should expect to obtain the hydroxide (AgOH) in this fashion, but it appears to be unstable. The aqueous solution of argentic oxide, however, is distinctly alkaline, and presumably therefore does contain the hydroxide: $2AgOH \rightleftarrows Ag_2O + H_2O$. Silver oxide is formed by boiling silver chloride with caustic potash. Since the oxide is much more soluble than the chloride (p. 544), we should expect the reverse of the above action to be the normal one. Here, however, the excess of potassium hydroxide (hydroxidion) represses the ionization of the silver hydroxide and reverses the relations in regard to solubility (*cf.* p. 585).

Argentic oxide melts and gives off its oxygen at 250–270°. It is an active basic oxide, and all the salts of silver are derived from it, the two other oxides having no corresponding salts. When moist, it absorbs

carbon dioxide from the air. Its solutions are said to show concentrations of hydroxidion much smaller, it is true, than equimolar solutions of the active bases, but considerably greater than similar solutions of ammonium hydroxide (p. 331). The oxide dissolves easily in ammonium hydroxide, and the ammonio-argentic hydroxide $Ag(NH_3)_2.OH$ which is formed is as active a base as is potassium hydroxide. The solution, when allowed to evaporate, deposits black crystals of an explosive substance whose composition has not been determined. This is "fulminating silver" (not to be confused with fulminate of silver Ag.ONC).

Silver **peroxide** Ag_2O_2 (*cf.* p. 308) is formed by the action of ozone on silver. In the electrolysis of silver nitrate it is deposited in shining black crystals on the positive electrode. There is also a **suboxide** Ag_4O.

Silver Nitrate. — This salt is obtained by treating silver with aqueous nitric acid:

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O.$$

From the solution, colorless rhombic crystals (Fig. 7, p. 13) isomorphous with those of potassium nitrate (Fig. 98, p. 557) are deposited. These melt at 218°. In the form of thin sticks made by casting (lunar* caustic), the substance is used in medicine, partly because it combines with albumins to form insoluble compounds. When commercial silver, containing copper, is used to make silver nitrate, the solution is evaporated to dryness and heated at 250° until the nitrate of copper has all been decomposed. At this temperature the silver salt is unaffected, and when cool can be separated from the insoluble cupric oxide by extraction with water.

The aqueous solution is neutral. The pure salt is not affected by light, but when deposited on cloth, on the skin of the fingers, or on the mouth of the reagent bottle, it is converted into the chloride, and from this, in turn, silver is liberated. For this reason it is an ingredient in marking-inks. The dry compound combines with ammonia, giving $AgNO_3,3NH_3$. In its aqueous solution ammonium hydroxide produces, first a faint precipitation of the oxide, and then the soluble complex salt $Ag(NH_3)_2.NO_3$.

Other Salts of Silver. — Silver **carbonate**, the neutral salt Ag_2CO_3, and not a basic carbonate is precipitated from solutions of salts of

* (Lat.) *luna* (the moon), the alchemical name for silver.

silver by soluble carbonates. It is slightly yellow in color. With water it gives a faint alkaline reaction, and, like calcium carbonate, is soluble in excess of carbonic acid (p. 594). When heated, the carbonate decomposes, leaving metallic silver. Other compounds of silver, for example, the chloride, when heated in a crucible with sodium carbonate give this salt by double decomposition, and hence are finally reduced to a button of metallic silver. The **sulphate** is made by the action of concentrated sulphuric acid on the metal. It is not very soluble in water, and crystallizes in rhombic prisms isomorphous with anhydrous sodium sulphate. When it is mixed with a solution of aluminium sulphate (*q.v.*), octahedral crystals of **silver-alum** $Ag_2SO_4, Al_2(SO_4)_3, 24H_2O$ are obtained. Silver **sulphide** is precipitated by hydrogen sulphide from solutions of all silver compounds, whether free acids are present or not, and irrespective of the form in which the silver is combined. Excess of potassium cyanide, however, prevents its precipitation from the argenticyanide. The sulphide is formed by the action of metallic silver on alkaline hydrosulphides, and this interaction forms the basis of the "hepar" test for sulphur (p. 391). Silver **orthophosphate** Ag_3PO_4 (yellow), **arsenate** Ag_3AsO_4 (brown), and **chromate** Ag_2CrO_4 (crimson), are produced by precipitation, and their distinctive colors enable us to use silver nitrate in analysis as a reagent for identifying the acid radicals.

Electroplating. — The process is similar to the electro-deposition of copper (p. 617). The article to be plated is cleaned with extreme care and attached to the negative wire. A plate of silver forms the positive electrode, and since simple salts of silver do not give coherent deposits, the bath is a solution of potassium argenticyanide. The kalion ($K^{\cdot}$) migrates to the negative wire, and since potassium requires a much greater E.M.F. for its liberation than does silver, silver is there deposited from the trace of argention given by the complex silver ions in the neighborhood:

$$Ag(CN)_2' \leftrightarrows Ag^{\cdot} + 2CN'$$
$$Ag^{\cdot} + \ominus \rightarrow Ag.$$

The potassium cyanide remains in solution. At the positive electrode silver goes into solution in equivalent amount giving argention, and the above equations are reversed.

Mirrors are silvered through the reduction of silver nitrate by organic compounds such as potassium-sodium tartrate (Rochelle salt),

glycerine, formaldehyde (formol), or sugar. On a small scale, dilute silver nitrate is mixed with ammonium hydroxide until the solution is clear, and then a little caustic potash, a few more drops of ammonia, and finally a very little glycerine, are added. A watch-glass floated on this mixture quickly acquires a deposit of silver.

Photography. — Bromo-gelatine dry plates are made by preparing an emulsion of gelatine to which silver nitrate and a slight excess of ammonium bromide have been added. After the emulsion has been kept warm until the precipitate of silver bromide has coagulated into small granules ("ripening"), it is allowed to solidify. It is then cut up, and the ammonium nitrate is washed out with water. After drying and remelting, the emulsion is finally applied to plates of glass. The excess of ammonium bromide and the ripening both increase the subsequent sensitiveness of the plates.

After exposure, often for only a fraction of a second, there is no visible alteration in the film. The image is **developed**. Chemically, this consists in reducing the silver bromide to metallic silver by means of reducing agents. While the whole of the halide upon the plate is reducible, if the reducing agent is kept upon it for a sufficient length of time, the parts reached by the light are affected *first*, and with a speed proportional to the intensity of the illumination undergone by each part. The reducing agent is poured off when sufficient "contrast" between the parts variously illuminated has been attained. The unreduced silver bromide is then dissolved out with sodium thiosulphate ("hyposulphite of soda" or "hypo"), and the silver image is thus saved from obliteration by the silver that would be deposited if the plate were to be brought into the light without this treatment (**fixing**). The result is a "negative," as the parts brightest in the object are now opaque, and the darkest parts of the object are transparent.

According to one view, the exposure reduces certain portions of the bromide to a sub-bromide, perhaps Ag_2Br, which is more easily reduced than silver bromide, and is consequently first attacked by the developer. The first particles of free silver then interact with neighboring molecules of AgBr, giving more Ag_2Br. Thus the reduction proceeds extensively wherever Ag_2Br is found and in proportion to its amount. The gelatine is the sensitizing substance, and promotes the dissociation of the silver bromide ($2AgBr \rightleftarrows Ag_2Br + Br$), which is a reversible action, by combining with the bromine. Potassium bromide, when added to

the developer, restrains the development, probably by rendering the silver bromide less soluble (*cf.* p. 583).

The simplest developer is potassium-ferrous oxalate $K_2.Fe(C_2O_4)_2$, a solution of which may be made by mixing ferrous sulphate and potassium oxalate. For the sake of simplicity we may regard the action as a reduction by means of ferrous oxalate, which itself is oxidized to ferric oxalate ($Fe_2(C_2O_4)_3$):

$$3FeC_2O_4 + 3Ag_2Br \rightarrow Fe_2(C_2O_4)_3 + FeBr_3 + 6Ag.$$

In brief, we have $3Fe^{II}$ becoming $2Fe^{III} + Fe^{III}$, and this amount of bivalent iron therefore takes up 3Br, liberating the silver with which it was combined. Other developers commonly employed are alkaline solutions of the sodium salts of hydroquinone and pyrogallic acid.

In **printing**, the light and dark are again reversed, the denser parts of the negative protecting the compounds on the paper below it from action, and leaving them white. Either "bromide" papers, which require only brief exposure and are developed like the plate, are used, or silver chloride is the sensitive substance, and prolonged exposure to light is allowed to liberate the proper amount of silver. The operation of fixing is performed as before. In **toning**, a solution of sodium chlor-aurate is employed. A portion of the silver dissolves, displacing gold (p. 362), which is deposited in its place:

$$NaAuCl_4 + 3Ag \rightarrow NaCl + 3AgCl + Au.$$

The thin film of gold gives a richer color to the print. In platinum toning, potassium chloroplatinite K_2PtCl_4 is similarly used.

Many other actions are utilized in photography. Thus, ferric oxalate is reduced by light to ferrous oxalate: $Fe_2(C_2O_4)_3 \rightarrow 2FeC_2O_4 + 2CO_2$. When paper coated with a solution of the former, or a mixture of ferric chloride and ammonium oxalate, is used for printing, the pale-yellow ferric salt loses its color where it has been turned into the ferrous salt. If the paper is then dipped in a solution of ferri-cyanide of potassium $K_3.Fe(CN)_6$ the ferrous salt precipitates the insoluble and deep-blue ferrous ferricyanide $Fe_3[Fe(CN)_6]_2$, while the unchanged ferric salt simply gives a soluble brown substance, which can be washed out. For regular **blue prints**, ammonium-ferric citrate is employed instead of the oxalate. If the above paper, after printing, is dipped in potassium chloroplatinite (or has been coated with this salt at the same time that it received the ferric oxalate), and is then

dipped in potassium oxalate solution, the latter dissolves the insoluble ferrous oxalate, and the potassium-ferrous oxalate reduces the platinum compound, giving a **platinum print**:

$$6FeC_2O_4 + 3K_2PtCl_4 \rightarrow 2Fe_2(C_2O_4)_3 + 2FeCl_3 + 3Pt + 6KCl.$$

We have already seen (p. 484) that light of short wave-length — blue and violet — has the greatest effect upon silver halides. The time, in seconds, required for equal effects is approximately: violet 15, blue 29, green 37, yellow 330, red 600. Hence objects showing to the eye a variety of colors are entirely misrepresented, as regards the relative brightness of their parts, by photography. Now the important fact, in this connection is, that only that part of the light which is absorbed in traversing the film, and not that which is scattered or transmitted, can be used for chemical change. Hence, dipping plates in solutions of substances capable of absorbing yellow and red radiations causes them to absorb more of the energy of these photographically weakest radiations, and to give greater chemical action in response to them. This partially restores the balance. Such plates are called **orthochromatic**, and are made with substances like eösin or cyanine.

Analytical Reactions of Silver Compounds. — The ion of salts of silver, argention $Ag^{\cdot}$, is colorless. Many of its compounds are insoluble, the precipitation of the chloride, which is insoluble in dilute acids, being used as a test. Mercurous chloride and lead chloride are also white and insoluble, but silver chloride dissolves in ammonium hydroxide, mercurous chloride (*q.v.*) turns black, and lead chloride, which is also soluble in hot water, is not altered in color. With excess of ammonium hydroxide, silver salts give the complex cation $Ag(NH_3)_2^{\cdot}$ and, from solutions containing silver in this form, only the iodide and sulphide can be precipitated. Sodium thiosulphate and potassium cyanide dissolve all silver salts, giving salts of complex acids with silver in the anion (p. 629). Zinc displaces silver from all forms of combination.

Gold.

Chemical Relations of the Element. — This element forms two very incomplete series of compounds corresponding respectively to aurous and auric oxides, Au_2O and Au_2O_3. The former is a feebly basic oxide, the latter mainly acid-forming. No simple salts

with oxygen acids are stable. All the compounds of gold are easily decomposed by heat with liberation of the metal. All other common metals displace gold from solutions of its compounds (p. 362). Mild reducing agents likewise liberate gold. The element enters into many complex anions (p. 536).

Occurrence and Metallurgy. — Gold is found chiefly in the free condition disseminated in veins of quartz, or mixed with alluvial sand. Small quantities are found also in sulphide ores of iron and copper. Telluride of gold (sylvanite), in which silver takes the place of part of the gold $[Au,Ag]Te_2$*, is found in Colorado. This mineral when heated loses its tellurium, and gold, alloyed with silver, remains.

From the alluvial deposits, gold is usually separated by washing in a cradle, as in the Klondyke. Quartz veins, which in the Transvaal Colony reach a thickness of a meter and carry an average of 18 g. of gold per ton, are mined, and the material is pulverized with stamping machinery. About 55 per cent of the gold is then separated by allowing the powdered rock to be carried by a stream of water over copper plates amalgamated with mercury. The gold dissolves in the latter, and is secured by removal and distillation of the amalgam. The finer particles contained in the sludge which runs off ("tailings"), are extracted by adding a dilute solution of potassium cyanide (MacArthur-Forest process) and exposing the mixture to the air. Oxidation and simultaneous interaction with the cyanide give potassium aurocyanide. Hydrogen peroxide, which is formed in many oxidations by free oxygen, is produced also:

$$2Au + 4KCN + 2H_2O + O_2 \rightarrow 2KAu(CN)_2 + 2KOH + H_2O_2,$$
$$2Au + 4KCN + H_2O_2 \rightarrow 2KAu(CN)_2 + 2KOH.$$

From this solution the gold is isolated, either by electrolysis, in which a plate of lead forms the cathode (and is subsequently cupelled. Siemens-Halske process), or in the form of a purple powder by precipitation with zinc.

Auriferous pyrites is washed, and then treated with chlorine gas. The chloride of gold which is formed is dissolved out with water. From

* Amongst minerals, mixed crystals of isomorphous salts are so commonly found that formulæ like the above are constantly used by mineralogists. $[Au,Ag]Te_2$ indicates a mixture in varying proportions of the isomorphous tellurides $AuTe_2$ and $AgTe_2$.

the solution, the gold is precipitated with ferrous sulphate or oxalic acid:

$$2AuCl_3 + 6FeSO_4 \rightarrow 2Fe_2(SO_4)_3 + 2FeCl_3 + 2Au,$$
$$2AuCl_3 + 3H_2C_2O_4 \rightarrow 6HCl + 6CO_2 + 2Au.$$

In the former case a purple powder, and in the latter, if the solution is heated, a spongy mass (the form used by dentists), is obtained.

The gold separated from ores in the above ways contains silver, copper, lead, and other metals, and various methods of refining, electrolytic and otherwise, are used. In one of these the gold is melted, and a stream of chlorine is passed through it. The metals, excepting gold, are converted into chlorides. The chloride of silver rises as a liquid to the surface, while chlorides of arsenic and antimony are volatilized. A layer of melted borax prevents loss of silver chloride by volatilization. The silver chloride, when it has solidified, is placed between wrought-iron plates and reduced by the action of dilute sulphuric acid upon the latter.

The world's production of gold during the first half of the nineteenth century averaged 27 tons annually. In 1897 it was 363 tons, and in 1899, 472.6 tons. In the former year North America, including Canada, produced 28.5 per cent of the whole, the Transvaal Colony 23.2 per cent, and Australia 21.2 per cent.

Properties of the Metal. — Gold is yellow in color, and is the most malleable and ductile of all the metals. It melts at 1064°. To give it greater hardness it is alloyed with copper, the proportion of gold being defined in "carats." Pure gold is "24-carat." British sovereigns are 22-carat and contain $\frac{2}{24}$ of copper. American, French, and German coins are 21.6-carat, or 90 per cent gold. Silver takes the place of copper in Australian sovereigns.

Gold is not affected by free oxygen or by hydrogen sulphide. It does not displace hydrogen from dilute acids, nor does it interact with nitric or sulphuric acids or any oxygen acids except selenic acid. It combines, however, with free chlorine, and it therefore interacts with a mixture of nitric and hydrochloric acids (*aqua regia*), which gives off this gas (p. 448). Chlorauric acid $H.AuCl_4 (= HCl,AuCl_3)$ is formed, and the action is assisted by the fact that the gold ions are taken into the little-dissociated anion $AuCl_4'$. Gold is the least active of the familiar metals.

Compounds with the Halogens. — **Chlorauric acid**, formed as above, is deposited in yellow, deliquescent crystals of $H.AuCl_4, 4H_2O$. The yellow sodium chloraurate $NaAuCl_4, 2H_2O$, obtained by neutralization of the acid, is used in photography (p. 634). The acid gives up hydrogen chloride when heated very gently, leaving the red, crystalline **auric chloride** $AuCl_3$. The tendency to form complex compounds is such, however, that when dissolved in water free from hydrochloric acid, this salt gives $H_2.AuCl_3O$. Red crystals of $H_2AuCl_3O, 2H_2O$ are deposited by the solution. When auric chloride is heated to 180° **aurous chloride** AuCl and chlorine are formed. This salt is a white powder. It is insoluble in water, but in boiling water is converted quickly into auric chloride and free gold: $3AuCl \rightarrow AuCl_3 + 2Au$. When potassium iodide is added to a solution of chlorauric acid, or to sodium chloraurate, the yellow **aurous iodide** is precipitated:

$$NaAuCl_4 + 3KI \rightarrow NaCl + AuI + I_2 + 3KCl.$$

The action is like that on cupric salts (p. 621), and for a similar reason, namely, that auric iodide is not stable.

Other Compounds. — When caustic alkalies are added to chlorauric acid, or to sodium chloraurate, **auric hydroxide** $Au(OH)_3$ is precipitated. This substance is an acid, and interacts with excess of the base, forming **aurates**. These are derived from met-auric acid ($Au(OH)_3 - H_2O = HAuO_2$), as, for example, potassium aurate $K.AuO_2, 3H_2O$. This salt interacts by double decomposition, giving, for instance, with silver nitrate, the insoluble silver salt $AgAuO_2$. Its solution is alkaline in reaction, a fact which shows that auric acid is a weak acid (*cf.* p. 344).

Auric oxide Au_2O_3 is a brown, and **aurous oxide** Au_2O is a violet powder. With hydrochloric acid the latter gives chlorauric acid and free gold.

On account of its reducing action, hydrogen sulphide precipitates from chlorauric acid a dark-brown mixture containing much **aurous sulphide** Au_2S and free sulphur, as well as some **auric sulphide** Au_2S_3. The sulphides interact with alkali sulphides, giving complex **sulphaurites** and **sulphaurates**, such as $K_3AuS_2(= 3K_2S, Au_2S)$ and $KAuS_2(= K_2S, Au_2S_3)$, which are soluble (p. 537, and see Tin, Arsenic, and Antimony).

The **aurocyanides**, like $K.Au(CN)_2(= KCN, AuCN)$, and the **auricyanides** like $K.Au(CN)_4(= KCN, Au(CN)_3)$, are formed by the action

of potassium cyanide on aurous and auric compounds respectively. They are colorless and soluble. Their solutions are used as baths, in conjunction with a gold anode, for electrogilding.

Analytical Reactions of Gold. — The metallic "streak," produced by rubbing the metal on touchstone (Lydian stone, a black basalt), is not easily removed by nitric acid of sp. gr. 1.36 (57.5 per cent). In assaying, the material containing the gold is heated with borax and lead in a small crucible (cupel) of bone-ash. The lead and copper are oxidized, and the oxides are absorbed by the cupel, leaving a drop of molten alloy of gold and silver. The cold button is flattened by hammering and rolling, and treated with nitric acid to remove the silver. The gold, which remains unattacked, is washed, fused again, and weighed. The acid will not interact with the silver and remove it completely if the quantity of gold exceeds 25 per cent. When the proportion of gold is greater than this, a suitable amount of pure silver is fused with the alloy ("quartation").

Exercises. — 1. How much copper will be deposited per hour on each sq. cm. of an electrode immersed in cupric sulphate solution when the current density is $\frac{1}{4}$ ampere per sq. cm. (p. 323)? How much copper would be obtained under the same conditions from a cuprous salt?

2. Write equations for the interactions (*a*) of salt water and oxygen with copper (p. 618), (*b*) of ferrous oxide and sand (p. 617), (*c*) of verdigris, arsenious acid, and acetic acid (p. 624).

3. Write the formulæ of the basic chloride, nitrate, carbonates, and sulphate of copper as if these substances were composed of the normal salt, the oxide and water (p. 618).

4. What may be the formula of the compound of cupric hydroxide and sodium tartrate (p. 623)?

5. Can you develop any relation between the facts that solutions of cupric salts are acid in reaction and that they give basic carbonates by precipitation?

6. Formulate the action of potassium cyanide in dissolving cupric hydroxide and cuprous sulphide, assuming that potassium cuprocyanide is formed.

7. How should you set about making cupric orthophosphate (in solution), ammonium cuprocyanide, and lead cuprocyanide?

8. Write the formulæ of some of the double salts analogous to potassium-cupric sulphate (p. 625).

9. What chemical agents are present in a Bunsen flame? If borax beads were made in the oxidizing flame with cupric chloride, cuprous bromide, and cupric sulphate, severally, what actions would take place?

10. If the solubility ratio of silver in zinc and in lead were 1000 : 1, and 2 per cent of zinc were used, what proportion of the total silver would be secured by Parke's method?

11. Which is more stable, silver sulphate or cupric sulphate, silver nitrate or cupric nitrate? To what salts are the silver compounds in this respect more closely allied?

12. Write the equations for the interaction of (*a*) silver and concentrated sulphuric acid, (*b*) silver chloride and sodium carbonate when heated strongly, (*c*) sodium thiosulphate and silver bromide, (*d*) potassium ferricyanide and ferrous oxalate.

13. What reagents should you use to precipitate the phosphate, arsenate, and chromate of silver?

14. Write the equations for the interactions of (*a*) gold and selenic acid, in which selenious acid is formed, (*b*) potassium hydroxide and auric hydroxide, (*c*) potassium cyanide and sodium chloraurate.

15. In what respects are the elements of this family distinctly metallic, and in what respects are they allied to the non-metals (p. 533)?

16. Collect all the evidence tending to show that the cuprous compounds are more stable than the cupric.

17. Describe in terms of the categories used by the phase rule the systems (*a*) cupric nitrate and water at 24.5° and (*b*) silver iodide at 146°.

18. Make a classified list of the methods by which cupric compounds are transformed into cuprous, and *vice versa*.

CHAPTER XXXVII

GLUCINUM, MAGNESIUM, ZINC, CADMIUM, MERCURY. THE RECOGNITION OF CATIONS IN QUALITATIVE ANALYSIS

The Chemical Relations of the Family. — The remaining elements of the third column of the periodic table, namely, glucinum or beryllium (Gl, or Be, at. wt. 9.1), magnesium (Mg, at. wt. 24.36), zinc (Zn, at. wt. 65.4), cadmium (Cd, at. wt. 112.4), and mercury (Hg, at. wt. 200.0), although all bivalent, do not form a coherent family. Glucinum and magnesium resemble zinc and cadmium, and differ from the calcium family, in that the sulphates are soluble, the hydroxides easily lose water leaving the oxides, the chlorides are comparatively volatile, and the metals are not rapidly rusted in the air and do not easily displace hydrogen from water. They resemble the calcium family, and differ from zinc and cadmium, in that the sulphides are hydrolyzed by water, the oxides are not reduced by heating with carbon, complex cations are not formed with ammonia, and the metals do not enter into complex anions. But glucinum differs from magnesium and resembles zinc in that its hydroxide is acidic as well as basic. This is not unnatural, since in the periodic system it lies between lithium, a metal, and boron, a non-metal. Mercury is the only member of the group that forms two series of compounds. These are derived (p. 278) from the oxides HgO and Hg_2O. Mercury approaches the noble metals in the ease with which its oxide is decomposed by heating, and in the position of the free element in the electromotive series.

The vapor densities of zinc, cadmium, and mercury show the vapors of these three metals to be monatomic.

The compounds of the metals of this family give no color to the borax bead.

GLUCINUM.

Chemical Relations of the Element. — Glucinum (or beryllium) is bivalent in all its compounds. Its oxide and hydroxide are basic, and are also feebly acidic towards active bases (see Zinc hydroxide).

On account of this fact and the extreme ease with which its carbonate gives up carbon dioxide, in both of which respects it resembles aluminium, it was first thought to be trivalent. This made its atomic weight 13.6, the amount combining with one chemical unit of chlorine being 4.55. In the periodic system, however, there was a space for a bivalent element with the atomic weight 9.1 (= 2 × 4.55) between lithium and boron, and none for a trivalent element. Later (1884) Nilson and Pettersson determined the vapor density of the chloride and of certain organic compounds of the element, and found only 9.1 parts of glucinum in the molar weights of the compounds. The element derives its name from the sweet taste of its salts (Gk. γλυκύς, sweet).

The Metal and its Compounds. — Glucinum occurs in beryl, a metasilicate of glucinum and aluminium $Al_2Gl_2(SiO_3)_6$. Specimens of beryl tinted green by the presence of a little silicate of chromium are known as emeralds. The metal may be obtained by electrolysis of the easily fusible double fluoride $GlF_2, 2KF$. In powdered form it burns when heated in the air. It displaces hydrogen from cold, dilute acids, and also, when heated, from caustic potash:

$$Gl + 2KOH \rightarrow K_2GlO_2 + H_2.$$

The oxide interacts with acids and with strong bases. The salts give no color to the Bunsen flame.

MAGNESIUM.

Chemical Relations of the Element. — Magnesium is bivalent in all its compounds. The oxide and hydroxide are basic exclusively. The element does not enter into complex cations or anions.

Occurrence. — Magnesium carbonate occurs alone as magnesite, and in a double salt with calcium carbonate $MgCO_3, CaCO_3$ as dolomite. The sulphate and chloride are found as hydrates and as constituents of double salts (see below) in the Stassfurt deposits. Silicates are also common. Olivine is the orthosilicate Mg_2SiO_4. Serpentine is a hydrated disilicate, $[Mg,Fe]_3,Si_2O_7, 2H_2O$, as is also meerschaum, and asbestos is an anhydrous silicate. The element derives its name from Magnesia, a town in Asia Minor.

The Metal. — Magnesium is manufactured by electrolysis of dehydrated and fused carnallite $MgCl_2,KCl, 6H_2O$. The iron crucible

in which the material is melted forms the cathode, and a rod of carbon the anode. The metal is silver-white, and when heated can be pressed into wire and rolled into ribbon. Commercial specimens of the latter often contain zinc.

Chemically the metal is less active than are the metals of the alkaline earths. It slowly becomes coated with a layer of the oxide. It displaces hydrogen from boiling water and, of course, from cold, dilute acids. Magnesium burns in air with a white light, rich in rays of short wave-length such as act upon photographic plates (p. 458). The ash contains the nitride Mg_3N_2, as well as the oxide. The presence of the former may be shown by the evolution of ammonia when the white powder is boiled with water (p. 417). When the metal is heated with the oxides of boron, of silicon, and of many of the metals, it combines with the oxygen and liberates the other element.

Powdered magnesium is used in pyrotechny, and, with potassium chlorate (10 : 17), in making flash-light powder for use in photography.

Magnesium Chloride. — This salt occurs in salt deposits as the hexahydrate $MgCl_2,6H_2O$, a highly deliquescent compound obtained also by evaporating an aqueous solution, and as carnallite $MgCl_2, KCl, 6H_2O$. The latter is an important source of potassium chloride (p. 551), and almost all the magnesium chloride combined with it is thrown away. When the hexahydrate is heated, a part of the chloride is hydrolyzed, some magnesium oxide remaining, and some hydrogen chloride being given off. Sea-water cannot be used in ships' boilers because of the hydrochloric acid liberated by the magnesium chloride which the water contains. The salt forms a double chloride with ammonium chloride $MgCl_2, NH_4Cl, 6H_2O$ which is isomorphous with carnallite, and this salt can be dehydrated without hydrolysis of the chloride. Afterwards the ammonium chloride can be volatilized (p. 421). To utilize natural magnesium chloride, the manufacture of chlorine from it, by passing air and steam over the salt at a high temperature, has been attempted:

$$4MgCl_2 + 2H_2O + O_2 \rightarrow 4MgO + 4HCl + 2Cl_2.$$

The Oxide and Hydroxide. — Magnesium oxide is made by heating the carbonate, and is known as "calcined magnesia." It is a white, highly infusible powder, and is used for lining electric furnaces and making crucibles. It combines slowly with water to form the hydroxide.

The hydroxide is found in nature as brucite. It is also precipitated from solutions of magnesium salts by alkalies. It is very slightly soluble in water, much less so than calcium hydroxide, but more so than are the hydroxides of zinc and the other heavy metals. The solution has a barely perceptible alkaline reaction.

Magnesium hydroxide is not precipitated by ammonium hydroxide when ammonium salts are present also. The ammonium salts, being highly ionized and giving a high concentration of ammonion $NH_4^{\cdot}$, repress the ionization of the feebly ionized ammonium hydroxide, and so reduce the concentration of hydroxidion which it furnishes. With the ordinary concentration of $Mg^{\cdot\cdot}$, therefore, the amount of hydroxidion existing in presence of excess of a salt of ammonium is too small to bring the solubility product $[Mg^{\cdot\cdot}] \times [OH']^2$ up to the value required for precipitation. Conversely, magnesium hydroxide interacts with solutions of ammonium salts and passes into solution:

$$\left.\begin{array}{l} Mg(OH)_2\,(\text{solid}) \rightleftarrows Mg(OH)_2\,(\text{diss'd}) \rightleftarrows Mg^{\cdot\cdot} + 2OH' \\ \qquad\qquad\qquad 2NH_4Cl \qquad\qquad \rightleftarrows 2Cl' + 2NH_4^{\cdot} \end{array}\right\} \rightleftarrows 2NH_4OH.$$

In presence of excess of ammonium chloride, the OH′ combines with $NH_4^{\cdot}$ to form molecular ammonium hydroxide, and the equilibria in the upper line are displaced forwards to generate a further supply of the former. With sufficiently great concentration of the ammonium chloride, all the magnesium hydroxide may thus dissolve; with only a small excess a condition of equilibrium with solid magnesium hydroxide is reached. The whole case is analogous to the interaction of acids with insoluble salts (p. 598). Magnesium *oxide* also dissolves in salts of ammonium. It gives first the hydroxide by interaction with the water.

Magnesium Carbonate. — The normal carbonate is found in nature. Only hydrated *basic* carbonates are formed by precipitation, and their composition varies with the conditions. The carbonate manufactured in large amounts and sold as *magnesia alba* is approximately $Mg_4(OH)_2(CO_3)_3 . 3H_2O$. The carbonates are not precipitated in the presence of ammonium salts, and interact with such salts in the same way as does the hydroxide.

Magnesium Sulphate. — The common heptahydrate $MgSO_4, 7H_2O$ crystallizes from cold water in rhombic prisms, and is called Epsom salts. At 0° a dodecahydrate appears. The heptahydrate is efflorescent, and loses its water by stages and with decreasing aqueous tension. The mono-

hydrate, found in the salt layers as kieserite $MgSO_4,H_2O$, has a very low aqueous tension, and is not rapidly dehydrated except above 200°. The hepta- and monohydrates present a striking case of difference in solubility in two forms of one salt, the former giving at 15° a solution containing 33.8 g. of the sulphate in 100 g. of water, while the latter is almost insoluble. Magnesium sulphate is used in the manufacture of sodium and potassium sulphates, and is employed also for "loading" cotton goods, and as a purgative.

Magnesium Sulphide. — The sulphide may be formed by heating the metal with sulphur. It is insoluble in water, but is decomposed and gives, finally, hydrogen sulphide and magnesium hydroxide:

$$2MgS + 2H_2O \leftrightarrows Mg(SH)_2 + Mg(OH)_2,$$
$$Mg(SH)_2 + 2H_2O \rightleftarrows Mg(OH)_2 \downarrow + 2H_2S.$$

The hydrolysis is more complete than in the case of calcium sulphide, and eliminates all the hydrogen sulphide, because magnesium hydroxide is much more insoluble than calcium hydroxide, and so there is little reverse interaction tending to reproduce the soluble hydrosulphide $Mg(SH)_2$.

Phosphates of Magnesium. — The only phosphate of importance is ammonium-magnesium orthophosphate $NH_4MgPO_4,6H_2O$, which appears as a crystalline precipitate when sodium phosphate and ammonium hydroxide are mixed with a solution of a magnesium salt. This compound is insoluble in water containing ammonium hydroxide, and is used in quantitative analysis for estimating both magnesium and phosphoric acid. Before being weighed the precipitate is ignited, and is thus converted into the anhydrous pyrophosphate of magnesium $Mg_2P_2O_7$. The salt $NH_4MgAsO_4,6H_2O$ has similar properties, and is used for estimating arsenic acid.

Analytical Reactions of Magnesium Compounds. — The magnesium ion is colorless and bivalent. It does not enter into complex ions. Soluble carbonates precipitate basic carbonates of magnesium, but not when ammonium salts are present. The latter limitation distinguishes compounds of magnesium from those of the calcium family. Potassium hydroxide precipitates the hydroxide of magnesium, except when salts of ammonium are present. The mixed phosphate of ammonium and magnesium, in presence of ammonium hydroxide, is the least soluble salt.

ZINC.

Chemical Relations of the Element. — Zinc is bivalent in all its compounds. Of these there are two sets, — the more numerous and important one in which zinc is the positive radical ($Zn.SO_4$, $Zn.Cl_2$, etc.), and a less numerous set, the zincates, in which zinc is in the negative radical ($Na_2.ZnO_2$, etc.). Both sets of salts are hydrolyzed by water, as the hydroxide is feeble whether it is considered as an acid or as a base. The element also enters into complex cations and anions. The salts are all poisonous.

Occurrence and Extraction from the Ores. — The chief sources of zinc are calamine or smithsonite $ZnCO_3$, zinc-blende (Ger. *blenden*, to dazzle) or sphalerite ZnS, franklinite $Zn(FeO_2)_2$, and zincite ZnO. The red color of the last is due to the presence of manganese.

The ores are first converted into oxide — the carbonate by ignition, and the sulphide by roasting. The sulphur dioxide is used to make sulphuric acid. A mixture of the oxide with coal is then distilled in earthenware retorts at 1300–1400°, the zinc condensing in earthenware receivers, while carbon monoxide burns at a small opening:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2,$$
$$ZnO + C \rightarrow CO + Zn.$$

At first zinc dust, a mixture of zinc and zinc oxide, collects in the receiver, and afterwards liquid zinc. The product, which is cast in blocks, is called spelter. It contains small amounts of lead, arsenic, iron, and cadmium, because the sulphides of these metals are almost invariably present in zinc-blende.

Properties and Uses of the Metal. — Zinc is a bluish-white crystalline metal. When cold it is brittle, but at 120–150° it can be rolled into sheets between heated rollers and then retains its pliability when cold. At 200–300° the metal becomes once more brittle, at 433° it melts, and at 920° it boils. The vapor density at 1740° is 2.64, and the molecular weight, therefore, 2.64×28.955 (p. 215) or 76.4. The gas is thus monatomic.

The metal burns in air with a bluish flame, giving zinc oxide. When cold it is not affected by dry air, but in moist air it is oxidized, and becomes covered with a firmly adhering layer of basic carbonate which protects it from further action. The metal displaces hydrogen from dilute acids, but with pure specimens the action almost ceases in

consequence of the formation of a layer of condensed hydrogen on the surface. Contact with a less electro-positive metal, such as lead, iron, copper, or platinum, enables the action to go on, because the hydrogen is then liberated at the surface of the other metal (see Electromotive chemistry). Crude zinc contains lead and iron and is therefore more active than pure zinc. Zinc also attacks boiling alkalies, giving the soluble zincate (see below): $2KOH + Zn \rightarrow K_2ZnO_2 + H_2$. The action on ammonium hydroxide is slower and different in nature:

$$Zn + 2NH_4OH + 2NH_3 \rightarrow Zn(NH_3)_4.(OH)_2 + H_2,$$

a complex cation being formed.

Sheet zinc, in consequence of its lightness (sp. gr. 7), is used in preference to lead (sp. gr. 11.5) for roofs, gutters, and architectural ornaments. Galvanized iron is made by dipping cleaned sheet iron in molten zinc. The latter, being more active (p. 362), is rusted instead of the iron. Zinc is used also in batteries and for making alloys (p. 619). It mixes in all proportions with tin, copper, and antimony, but with lead (p. 627) and with bismuth separation into two layers occurs, each metal dissolving only a little of the other. The two different modes of behavior resemble those of alcohol and water (p. 136) and ether and water (p. 147) respectively.

Zinc Chloride. — This salt is usually manufactured by treating zinc with excess of hydrochloric acid, evaporating the solution to dryness, and fusing the residue. When hydrochloric acid is thus present, the chloride $ZnCl_2$ is obtained. Evaporation of the pure aqueous solution, which is acid in reaction, results in considerable hydrolysis and formation of much of the basic chloride Zn_2OCl_2:

$$ZnCl_2 + H_2O \rightleftarrows HCl + Zn(OH)Cl, \quad (1)$$

$$2Zn(OH)Cl \rightarrow Zn_2OCl_2 + H_2O. \quad (2)$$

The salt is used in solid form as a caustic and, by injection of a solution into wood (*e.g.*, railway sleepers), as a poison to prevent the growth of organisms which promote decay. In both cases the salt combines with albumins, forming solid products. The aqueous solution, being acid, is employed also for dissolving the oxides from surfaces which are to be soldered. The acid is reproduced by hydrolysis as fast as it is used, and finally the oxychloride remains (equation 1 above).

Zinc Oxide and Hydroxide and the Zincates. — The **oxide** is obtained as a white powder by burning zinc or by heating the precipitated basic carbonates. It turns yellow when heated, recovering its whiteness when cold, in the same way that mercuric oxide is brown whilst hot and bright red when cold. It is employed in making a paint — zinc-white or Chinese white — which is not darkened by hydrogen sulphide. For filling teeth, dentists sometimes use a paste made by mixing the oxide with a strong solution of zinc chloride. It quickly sets to a hard mass of oxychloride.

The **hydroxide** of zinc appears as a white, flocculent solid when alkalies are added to solutions of zinc salts. It interacts as a basic hydroxide with acids, giving salts of zinc:

$$Zn(OH)_2 + H_2SO_4 \rightleftarrows Zn.SO_4 + 2H_2O.$$

It also interacts with excess of the alkali employed to precipitate it, giving a soluble **zincate**:

$$H_2ZnO_2 \uparrow + 2KOH \rightleftarrows K_2.ZnO_2 + 2H_2O.$$

Both actions are reversible, and the second requires a considerable excess of alkali for its completion: in fact, most of the zinc hydroxide seems to be simply in colloidal solution. From a consideration of these facts it is evident that zinc hydroxide when in solution is ionized both as an acid and as a base:

$$\begin{array}{c} 2H^{\cdot} + ZnO_2'' \rightleftarrows Zn(OH)_2\,(\text{diss'd}) \rightleftarrows Zn^{\cdot\cdot} + 2OH' \\ \downarrow\uparrow \\ Zn(OH)_2\,(\text{solid}) \end{array}$$

The ionization as an acid is less than that as a base, but both are small. Addition of an acid like sulphuric acid, however, furnishes hydrion; the hydroxyl ions combine with this to form water, and all the equilibria are displaced to the right. With a base, on the other hand, the hydrion is removed and the basic ionization simultaneously repressed, so that the equilibria are displaced to the left.

Zinc hydroxide interacts with ammonium hydroxide, giving a soluble complex compound with ammonia $Zn(NH_3)_4.(OH)_2$. The case is like those of copper (p. 623) and silver hydroxides (p. 631), and not like that of magnesium hydroxide (p. 644).

Compounds of zinc, when heated in the Bunsen flame with a salt of cobalt, gives a zincate of cobalt (Rinmann's green) $CoZnO_2$.

Hydrogen sulphide precipitates zinc sulphide from solutions of zincates and from solutions containing ammonia, so that some zinc ions $Zn^{\cdot\cdot}$ are present in both.

Carbonate of Zinc. — The normal zinc carbonate may be precipitated by means of sodium bicarbonate:

$$ZnSO_4 + 2NaHCO_3 \rightarrow Na_2SO_4 + ZnCO_3 + H_2O + CO_2.$$

The normal carbonate of sodium, however, gives basic carbonates, which, as in the case of magnesium (p. 644), vary in composition according to the conditions.

Zinc Sulphate. — This salt is formed when zinc-blende is roasted. It gives rhombic crystals of the hydrate $ZnSO_4, 7H_2O$. This, and the corresponding compounds of magnesium $MgSO_4, 7H_2O$, of iron $FeSO_4, 7H_2O$, and of several other bivalent metals, are all isomorphous, and are known as **vitriols**. The zinc salt is white vitriol. Like Epsom salts, it is dehydrated by stages, the last molecule of water being difficult to remove. It is used in cotton-printing and as an eye-wash ($\frac{1}{8}$ per cent solution).

The salt gives double salts with potassium and ammonium sulphate, of the form $ZnSO_4, K_2SO_4, 6H_2O$, which crystallize in the monosymmetric system, and are isomorphous with each other, and with double salts containing copper (p. 625), mercury (Hg^{II}), iron (Fe^{II}), magnesium, and other bivalent elements in place of the zinc. These compounds, unlike the complex cyanides, are almost completely decomposed in dilute solution (*cf.* p. 537).

Zinc Sulphide. — This compound is the only familiar sulphide which is white. The yellow color of zinc-blende is caused by the presence of sulphide of iron. Zinc sulphide is more soluble in water than is sulphide of copper, and hence it interacts with excess of strong acids, and passes into solution. It is not soluble enough, however, to be much affected by weak acids like acetic acid. This sort of behavior is shown also by calcium oxalate (p. 598), and was discussed fully in that connection. Zinc sulphide is thus capable of being precipitated when acetic acid is present, or when hydrogen sulphide is led into a solution of the acetate of zinc:

$$Zn(C_2H_3O_2)_2 + H_2S \rightleftarrows ZnS\downarrow + 2HC_2H_3O_2.$$

But when an active acid is present, or is formed during the operation, the sulphide is precipitated incompletely or not at all, the action being highly reversible :

$$ZnSO_4 + H_2S \rightleftarrows ZnS + H_2SO_4.$$

There are thus two ways of obtaining the sulphide by precipitation. A soluble sulphide causes it to be thrown down completely because no acid is liberated in the action :

$$ZnCl_2 + (NH_4)_2S \rightleftarrows ZnS\downarrow + 2NH_4Cl.$$

The other method is to add sodium acetate to the solution of the salt, and then lead in hydrogen sulphide. The acid which is liberated by the action upon the salt interacts with the sodium acetate, giving a neutral salt of sodium and acetic acid, and the zinc sulphide is not affected by the latter. In terms of the ionic hypothesis, the hydrion, liberated as the hydrogen sulphide interacts with the zinc salt, combines with acetanion introduced by the sodium acetate, and gives the little-ionized acetic acid.

Analytical Reactions of Zinc Salts. — Zinc sulphide is precipitated by the addition of ammonium sulphide to solutions of zinc salts and of zincates. Sodium hydroxide gives the insoluble hydroxide, which, however, interacts with excess of the alkali, giving the soluble zincate of sodium. Compounds of zinc, when heated on charcoal with cobalt nitrate, give Rinmann's green (p. 648).

Cadmium.

Chemical Relations of the Element. — This element is bivalent in all its compounds. Its oxide and hydroxide are basic exclusively, and the salts are not hydrolyzed by water. It enters into complex compounds having the ions $Cd(NH_3)_4^{\cdot\cdot}$, $Cd(CN)_4''$, and CdI_4''.

The Metal. — Aside from the rare mineral greenockite CdS, cadmium is found only in small amounts, as carbonate and sulphide, in the corresponding ores of zinc. During the reduction, being more volatile than zinc, it distils over first.

In color the metal resembles tin, and is much more malleable and ductile than zinc. It melts at 320° and boils at 770°.

It displaces hydrogen from dilute acids but is itself displaced from solutions of its compounds by zinc, since it is less electro-positive.

Compounds of Cadmium. — The **chloride** crystallizes as a dihydrate $CdCl_2, 2H_2O$, which is efflorescent and is not hydrolyzed during dehydration or in solution. Zinc chloride (p. 647) is deliquescent and is easily hydrolyzed. The halides are less ionized than are the corresponding compounds of most other metals. The **iodide**, in particular, seems to exist in solution as $Cd.CdI_4$, and the complex anion gives little ionic cadmium. On account of this fact even the sulphide cannot be precipitated completely from a solution of the iodide. Conversely, hydriodic acid dissolves the sulphide to a much greater extent than do other acids (see below).

The **hydroxide** is made by precipitation, and interacts, as a basic oxide, with acids, but not at all with bases. It dissolves in ammonium hydroxide, however, forming $Cd(NH_3)_4.(OH)_2$. The **oxide** is a brown powder, obtained by heating the hydroxide, carbonate, or nitrate, or by burning the metal.

The **sulphate** crystallizes from solution as $3CdSO_4, 8H_2O$, and is not isomorphous with the sulphates of zinc and magnesium. Soluble carbonates throw down the **normal carbonate** of cadmium $CdCO_3$, and not a basic carbonate.

Hydrogen sulphide precipitates the yellow **sulphide** CdS even from acid solutions of the salts. The substance is used as a pigment. Since zinc sulphide is not formed under these conditions (p. 650), the first part of the distillate from the reduction of the ore can be dissolved in hydrochloric acid and the cadmium precipitated as sulphide, while the zinc remains in solution. The sulphide of cadmium, however, is less insoluble in water than are the sulphides of copper and mercury, and therefore cannot be precipitated from a strongly acid solution. We have thus a distinct gradation in the solubility in water of various insoluble sulphides. The order of increasing insolubility, and consequent difference in behavior towards acids, is:

Barium, strontium, calcium, and magnesium sulphides:	attacked by water, and all acids.
Ferrous sulphide:	attacked even by acetic acid, but not by water.
Zinc sulphide:	attacked by dilute active acids, but not by acetic acid.
Cadmium sulphide:	attacked by concentrated active acids, but not by dilute acids.
Cupric sulphide:	attacked by fairly concentrated, actively oxidizing acids, like nitric acid, but not much by ordinary active acids.
Mercuric sulphide:	hardly attacked at all, even by hot nitric acid.

Analytical Reactions of Cadmium Compounds. — The cadmium ion $Cd^{\cdot\cdot}$ is bivalent and colorless. The yellow cadmium sulphide is precipitated by hydrogen sulphide, even from acid solutions of the salts. It is also precipitated from solutions containing the complex cation $Cd(NH_3)_4^{\cdot\cdot}$ and the complex anion $Cd(CN)_4''$, as, for example, from a solution made by adding excess of potassium cyanide to cadmium chloride solution ($K_2.Cd(CN)_4$). The latter property enables cadmium to be separated from copper (p. 624). The white hydroxide is thrown down by sodium hydroxide, and is not soluble in excess of this reagent. It is not formed from solutions containing the $Cd(NH_3)_4^{\cdot\cdot}$ and $Cd(CN)_4''$ ions, and dissolves in ammonium hydroxide. These and other precipitations are not complete when cadmium iodide $Cd.CdI_4$ is used.

MERCURY.

Chemical Relations of the Element. — Like copper, this element enters into two series of compounds, the mercurous and the mercuric, in which it is univalent and bivalent respectively. The mercurous halides, like the cuprous halides (and the argentic halides), are insoluble in water and are decomposed by light. There are, however, mercurous as well as mercuric salts of oxygen acids. Both of the oxides, Hg_2O and HgO, are basic exclusively, but in a feeble degree. The hydroxides, like silver hydroxide, are not stable, and lose water, giving the oxides. The salts of both sets are markedly hydrolyzed by water, and basic salts are therefore common. No carbonate is known. Mercury enters into the anions of a number of complex salts, such as $HgCl_4''$, HgI_4'', $Hg(CN)_4''$, etc. It does not give complex cations with ammonia resembling those of cadmium, copper, and silver ($Cd(NH_3)_4^{\cdot\cdot}$, etc.), from which ammonia is removed by heating, but instead forms a class of mercur-ammonium compounds like $Hg^{II}NH_2Cl$, all of which are insoluble. The mercuric halides and cyanide show many peculiarities due to their being very little ionized. Salts as a class are highly ionized bodies, and those of mercury and, to a less degree, those of cadmium are the only conspicuous exceptions.

The mercury salts of volatile acids, like the corresponding salts of ammonium (p. 421), can all be volatilized completely. Mercury vapor and all mercury compounds are poisonous, the soluble ones more markedly so than the insoluble ones.

The mercurous salts, as a rule, are formed when excess of mercury is employed, and mercuric salts when excess of the oxidizing acid or

other substance is present. Reducing agents turn mercuric into mercurous salts, and oxidizing agents do just the reverse.

As in the case of the cuprous compounds, it is a question whether simple or multiple formulæ, HgCl or Hg_2Cl_2, etc., should be employed for mercurous salts. Pending the discovery of some basis for a decision, the simple formulæ are used here.

Occurrence and Isolation of the Metal. — Mercury occurs to some extent native and to a larger extent as red, crystalline cinnabar, mercuric sulphide HgS. The chief mines are in Spain, California, and Austria.

The liberation of the metal is easy, because the sulphide is decomposed at a high temperature, and the sulphur forms sulphur dioxide. The mercury does not unite with oxygen, for the oxide decomposes (p. 12) at 400–600°:

$$HgS + O_2 \rightarrow Hg + SO_2.$$

In some places the ore is spread on perforated brick shelves in a vertical furnace, and the gases pass through tortuous flues in which the vapor of the metal condenses. The product is filtered through chamois-skin. For separation from metallic impurities, like zinc, arsenic, and tin, which are dissolved, it must be distilled. In the laboratory, where mercury finds many applications, it becomes impure with use, and then adheres to glass, and does not run freely in spherical droplets. For purification it is placed along with a little diluted nitric acid in a separatory funnel (Fig. 56, p. 147), and kept in continual agitation by means of a current of air drawn or blown through the mass. By this treatment foreign metals, such as sodium or zinc, nearly all of which are much more active than mercury (*cf.* p. 362), are converted into nitrates. Pure, dry mercury can be drawn off, when needed, at the bottom. If a high degree of purity is required, the product must be distilled *in vacuo*.

Physical Properties. — Mercury or quicksilver (NL. *hydrargyrum*, from Gk. ὕδωρ, water, and ἄργυρος, silver) is a silver-white liquid. At − 39.5° it freezes, and at 357° it boils. At ordinary temperatures it has a measurable vapor tension, at 15° 0.0008 mm. and at 99° 0.26 mm. The vapor is colorless, does not conduct electricity, and is monatomic. A gold-leaf suspended over mercury becomes amalgamated, since the solution of gold in mercury has a vapor tension smaller than that of pure mercury (p. 161).

Corrosive sublimate, when taken internally, is extremely poisonous. A very dilute solution is used in surgery to destroy lower organisms and thus prevent infection of wounds. The pharmaceutical tabloids of mercuric chloride contain sodium chloride, because, although the latter diminishes the activity of the compound, it also does away with the formation of insoluble chlorides and hastens solution. Mercuric chloride acts also as a preservative of zoölogical materials, forming insoluble compounds with albumins, and preventing their decay. For the same reason, albumin (white of an egg) is given as an antidote in cases of sublimate poisoning.

The Iodides of Mercury. — **Mercurous iodide** is formed by rubbing iodine with excess of mercury. It also appears as a greenish-yellow precipitate when potassium iodide is added to a solution of a mercurous salt. The compound decomposes spontaneously into mercury and mercuric iodide. The decomposition is much hastened by the use of excess of potassium iodide, which combines with and removes the mercuric iodide (see below):

$$2HgI \rightleftarrows Hg + HgI_2.$$

Mercuric iodide is obtained by direct union of mercury with excess of iodine, or by addition of potassium iodide to a solution of a mercuric salt. It is a scarlet powder, insoluble in water, but soluble in alcohol and ether. It interacts with excess of potassium iodide, forming the soluble, colorless potassium mercuri-iodide $K_2.HgI_4$ with which many precipitants fail to give mercury compounds. When heated above 116.5° it turns slowly into a yellow modification, and at 223° this new form melts. On being cooled, it freezes first in the tetragonal yellow form, and below 116.5°, especially if touched with a glass rod, it changes into the red, monoclinic variety with evolution of heat. Sulphur (p. 368) and ammonium nitrate (p. 565) show similar transition points. When the vapor of the compound is cooled, it first forms thin scales of the yellow form, which is the unstable one at low temperatures, and these turn red when touched. Similarly, precipitation gives first the yellow variety, which presently becomes red (*cf.* Transformation by steps, p. 453).

The Oxides. — When bases are added to solutions of mercurous salts, a brownish-black powder is thrown down, which, when dried, is found to be **mercurous oxide** Hg_2O. The hydroxide is doubtless

formed transitorily and then loses water (*cf.* Silver oxide, p. 630). Under the influence of light or gentle heat (100°), this compound resolves itself into mercuric oxide and mercury.

Mercuric oxide is formed as a red, crystalline powder, when mercury is heated in air near to 357°, but is usually made by decomposing the nitrate. Commercial specimens, incompletely decomposed, thus frequently give some nitric oxide when heated. It is formed also as a yellow powder by adding bases to solutions of mercuric salts. It is contended by some chemists that the difference in activity between the red and yellow forms is due solely to the finer state of division of the latter, and by others it is maintained that the substance is dimorphous (p. 369) and that two distinct varieties exist.

The Nitrates. — The **mercurous** salt is formed by the action of cold, diluted nitric acid upon excess of mercury. It forms monoclinic crystals of a hydrate $HgNO_3,H_2O$. It is hydrolyzed, slowly by cold, and rapidly by warm water, giving a basic nitrate:

$$2HgNO_3 + H_2O \rightleftarrows HNO_3 + Hg_2(OH)NO_3 \downarrow .$$

On this account a clear solution can be made only when some nitric acid is added. Free mercury is also kept in the solution to reduce mercuric nitrate, which is formed by atmospheric oxidation:

$$Hg(NO_3)_2 + Hg \rightarrow 2HgNO_3 \quad \text{or} \quad Hg^{\cdot\cdot} + Hg \rightarrow 2Hg^{\cdot}.$$

Mercuric nitrate is produced by using excess of warm, concentrated nitric acid. It forms rhombic tables of $Hg(NO_3)_2, 8H_2O$. The aqueous solution is strongly acid, and deposits a yellowish, crystalline, basic nitrate $Hg_3(OH)_2O(NO_3)_2$. The action is reversed by adding nitric acid.

Sulphides of Mercury. — **Mercurous sulphide** Hg_2S is formed by precipitation from mercurous salts, but is stable only below −10°. Above this temperature it decomposes into mercury and mercuric sulphide.

Crystallized **mercuric sulphide** occurs as cinnabar, and is red. When formed by precipitation with hydrogen sulphide, or by rubbing together mercury and sulphur, it is black and amorphous. By sublimation, in the course of which it dissociates, the black form gives the red, crystalline one. When allowed to stand under a solution of sodium sulphide, the black form is slowly transformed into the red. This

shows that, as we should expect, the red form is the more stable, possesses less energy, and is less soluble at ordinary temperatures. The change is effected by intermediate formation of a complex sulphide, the solution, when saturated toward the less stable black sulphide, being supersaturated toward the more stable red one. A white, crystalline sodium mercuri-sulphide $Na_2HgS_2, 8H_2O$ can, in fact, be obtained from the solution.

The black and the red varieties do not interact with concentrated acids, and are even unaffected by boiling nitric acid, which oxidizes most sulphides readily. They are, therefore, less soluble in water than cupric sulphide (pp. 600, 651), and much less so than sulphide of cadmium. They are attacked, however, by *aqua regia*.

The red form of the sulphide is used in making paint (**vermilion**). The color is more permanent than that of red lead (Pb_3O_4), because reducing gases (*e.g.* SO_2), acids (*e.g.* H_2SO_4), and hydrogen sulphide, which are present in the air, do not affect it. It is not stable, however, when applied to metals, since iron, zinc, etc., all displace mercury from combination, and in these cases, therefore, red lead is preferred.

Mercuric Cyanide. —This salt is made by treating precipitated mercuric oxide with hydrocyanic acid, and is obtained in square-prismatic crystals. When heated it gives off cyanogen: $Hg(CN)_2 \rightarrow Hg + C_2N_2$, and is a convenient source of this gas (p. 507). The compound is soluble in alcohol, ether, and water. In solution in water it is so little ionized that the freezing-point of the solution is normal (p. 292), and many reagents fail to show the presence of either ion. Thus, with silver nitrate no silver cyanide is precipitated, and with a base no mercuric oxide. With potassium cyanide it forms a complex cyanide $K_2.Hg(CN)_4$. Hydrogen sulphide throws down the sulphide from both the simple and the complex cyanides.

The Fulminate and Thiocyanate. — Mercuric fulminate $Hg(ONC)_2$ is obtained as a white precipitate when mercury is treated with nitric acid, and alcohol is added to the solution. It decomposes suddenly when struck, and is used in making percussion caps. The thiocyanate $Hg(SCN)_2$ is precipitated when potassium thiocyanate $K(SCN)$ is added to a solution of a mercuric salt. When formed into little balls and burned in the air, the substance leaves a curiously voluminous ash ("Pharaoh's serpents").

Mercur-ammonium Compounds. — When ammonium hydroxide is added to a solution of a mercuric salt, a white substance, of a type which we have not previously encountered, is thrown down. Mercuric chloride gives $HgNH_2Cl$, commonly called "infusible white precipitate," and the nitrate gives $HgNH_2NO_3$:

$$HgCl_2 + 2NH_3 \rightarrow HgNH_2Cl + NH_4Cl.$$

The substance may be regarded as being derived from ammonium chloride (p. 421) by the displacement of 2H by Hg:

$$Hg : N \begin{matrix} \diagup H \\ - H. \\ \diagdown Cl \end{matrix}$$

It would thus be named mercur-ammonium chloride.

When the mercuric chloride is added to a boiling solution of ammonium chloride containing ammonium hydroxide, mercur-diammonium chloride $Hg(NH_3Cl)_2$, "fusible white precipitate," appears.

The addition of ammonium hydroxide to a solution of potassium mercuri-iodide K_2HgI_4 gives rise to a third type of compound, dimercur-ammonium iodide Hg_2NI, H_2O, which appears as a brown precipitate:

$$2HgI_2 + 4NH_3 \rightarrow Hg_2NI + 3NH_4I.$$

A solution of potassium mercuri-iodide containing potassium hydroxide, **Nessler's reagent**, becomes distinctly yellow with traces of ammonia, and brown with larger amounts, and is, therefore, a valuable reagent for detecting traces of this base.

When calomel is treated with ammonium hydroxide, it turns into a black, insoluble body. This appears to be a mixture of free mercury, to which it owes its dark color, and "infusible white precipitate," $Hg + HgNH_2Cl$. To this reaction calomel owes its name (Gk. καλομέλας, beautiful black). Mercurous nitrate gives a black, insoluble mixture, $Hg + HgNH_2NO_3$. Calomel, when *dry*, absorbs ammonia gas, forming a molecular compound of the common type $HgCl, NH_3$. This substance loses the ammonia again when the pressure is reduced. The other compounds described above, on the other hand, do not contain nitrogen and hydrogen in the proportions necessary to form ammonia and are stable. Hence they are necessarily to be regarded as belonging to a different type.

Analytical Reactions of Mercury Compounds. — The two ionic forms of the element, monomercurion $Hg^{\bullet}$ and dimercurion $Hg^{\bullet\bullet}$, are

both colorless, but their chemical behavior is entirely different. Both give the black sulphide HgS, which is insoluble in acids and other solvents of mercury salts. Monomercurion gives the insoluble, white chloride, the black oxide, and a black mixture with ammonium hydroxide. Dimercurion gives a soluble chloride, a yellow, insoluble oxide, and a white precipitate with ammonium hydroxide. The behavior with stannous chloride (p. 655) is characteristic of mercuric salts. With potassium iodide the behavior of the two ions is quite different (p. 656). The more active metals displace mercury from all compounds. This displacement is employed as a test for compounds of mercury. Copper is used by preference as the displacing metal because the mercury is easily seen on its surface.

Salts of mercury are volatile. When heated in a tube with sodium carbonate, they also give a sublimate of metallic mercury.

The Recognition of Cations in Qualitative Analysis.

"Wet-way" analysis consists in recognizing the various positive and negative ions present in a solution (p. 343). In discussing hydrogen sulphide (p. 375), it was stated that the sulphides might be divided into three classes according to their behavior towards water and acids. Now these differences in behavior furnish us with a basis for distinguishing the cations present in a solution. Since the properties of a number of sulphides and other compounds of the metals have been studied in recent chapters, it is possible to make a more complete statement.

The following plan, taken in conjunction with the statements in the context, shows how a single cation may be identified, and how, when several cations are present, a separation preparatory to identification may be effected. What will be said applies only to the case of a *solution* containing salts like the chlorides, nitrates, or sulphates of one or more cations, and leaves the oxalates (p. 601), phosphates, cyanides, and some other salts, out of consideration.

Group 1. — It is usual to **add, first, hydrochloric acid**, to find out whether cations giving insoluble chlorides are present. Argentic, mercurous, and plumbic salts give the white $\mathbf{AgCl}$, $\mathbf{HgCl}$, and $\mathbf{PbCl_2}$ respectively. (For the further recognition of each, see p. 635.) Filtration eliminates the precipitate, if there is any.

Group 2. — A free, active acid being now present, **hydrogen sulphide is led** into the solution. The sulphides insoluble in active acids,

namely, **HgS, CuS, PbS, Bi_2S_3, CdS, As_2S_3, Sb_2S_3, SnS**, are therefore thrown down. The first four are black or brown, the next two are yellow, and the last two are orange and brown respectively. A dark-colored substance will naturally obscure one of lighter color, if more than one is present. If too much acid is used, the precipitation of several of the sulphides will be incomplete (p. 651); if too little, zinc sulphide may come down (p. 649). Filtration again eliminates the precipitate.

This group is easily subdivided. Any or all of the last three sulphides will pass into solution when warmed with yellow ammonium sulphide, for they give soluble complex sulphides similar to potassium sulphaurate (p. 638). The first five sulphides, or any of them, will be unaffected. On the other hand, these five sulphides, with the exception of HgS, will interact with hot nitric acid (p. 658). Other reactions described in the context are then used to distinguish between, or, if there is a mixture, to separate, the members of the sub-groups.

Group 3. — The solution (filtrate) is now neutralized with ammonium hydroxide, and **ammonium sulphide** is added. Some **ammonium chloride** is also used, to prevent the precipitation of magnesium hydroxide (p. 644), which, in any event, would be incomplete. The sulphides which are insoluble in water, and are not hydrolyzed by it, now appear. They are **FeS, CoS, NiS**, all black, **MnS, H_2O**, and **ZnS**, which are pink and white respectively. There are precipitated also the hydroxides of chromium and of aluminium, **$Cr(OH)_3$** and **$Al(OH)_3$**, because, although their sulphides are hydrolyzed by water, the hydroxides are formed by the hydroxidion in the ammonium sulphide solution. They are too insoluble to behave like magnesium hydroxide (p. 646) by dissolving in salts of ammonium. They also form no complex metal-ammonia ion, as does zinc (p. 648). The sulphides of nickel and cobalt resemble the sulphide of zinc in being precipitated by hydrogen sulphide when acetic acid is the only acid present. The other sulphides interact even with acetic acid (p. 651).

Another plan is to oxidize the iron, if present, and use ammonium chloride and ammonium hydroxide instead of ammonium sulphide. The hydroxides of the trivalent elements, $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, can be precipitated by excess of ammonium hydroxide even when salts of ammonium are present. Those of the bivalent metals, $Mn(OH)_2$, $Fe(OH)_2$, $Zn(OH)_2$, $Ni(OH)_2$, $Co(OH)_2$, resemble magnesium hydroxide (p. 644), and, of these, the last three resemble *also* zinc hydroxide (p. 648), and so cannot be precipitated. After filtration, ammonium

sulphide now throws down the sulphides of the five bivalent metals (for a third plan, see Chemical relations of aluminium).

Group 4. — After filtration from members of the iron group, if any were present, **ammonium carbonate** is added, and precipitates the remaining metals whose carbonates are insoluble, $BaCO_3$, $SrCO_3$, $CaCO_3$, with the exception of magnesium (p. 644).

By addition of **sodium phosphate** to a portion of the filtrate, magnesium, if present, now comes out in the form NH_4MgPO_4. There remain in solution only salts of **potassium, sodium, and ammonium**. Since only ammonium compounds, and other substances which can be volatilized have been added, evaporation and ignition of the residue leaves the salts of the two metals. If no other metallic elements have been shown to be present, it saves time to examine a fresh portion of the original material. Salts of ammonium must also be sought in a fresh sample by the usual test (p. 421).

The following simple compounds are soluble, but are so little ionized that their solutions do not show all the reactions of both of the ions: NH_4OH, H_2S, HNC, H_2CO_3, $HgCl_2$, $Hg(CN)_2$, $Fe(CNS)_3$, $Fe(C_2H_3O_2)_3$. With a number of others, for example CdI_2, the actions are incomplete for the same reason. Complex compounds, as we have seen, give complex ions, and the latter are usually so little resolved into simpler ions that the latter cannot be discovered by all the usual tests. Thus: $K.Ag(CN)_2$ gives $K^{\cdot}$ and $Ag(CN)_2'$, but very little $Ag^{\cdot}$ and CN' (p. 629); $Cu(NH_3)_2.Cl_2$ gives much $Cu(NH_3)_2^{\cdot\cdot}$, and Cl' but very little $Cu^{\cdot\cdot}$. The individual cases are fully described in the context.

Exercises. — 1. What is the numerical value (*a*) of the solubility product of magnesium hydroxide, (*b*) of the concentration of hydroxidion given by it and by normal ammonium hydroxide respectively (p. 544)? Will normal concentration of ammonium chloride suffice to reduce the latter below the former?

2. Why should we, perhaps, expect ammonium sulphide solution to precipitate magnesium hydroxide, and why does it not do so?

3. What volume of air is required to oxidize one formula-weight of zinc sulphide to ZnO and SO_2, and what volume of sulphur dioxide is produced? Is the product more or less diluted with nitrogen than when pure sulphur is burned, and by how much?

4. Make equations showing (*a*) the effect of heating zinc chloride with cobalt nitrate ($Co(NO_3)_2$) in the Bunsen flame (p. 648), (*b*) the

action of hydrogen sulphide on sodium zincate, (*c*) the actions of concentrated nitric acid and of concentrated sulphuric acid on mercury.

5. What is the distinction between a solid isomorphous mixture of two salts and a double salt ?

6. What kind of salts might take the place of sodium acetate in the precipitation of zinc sulphide (p. 650) ? Give examples.

7. Compare the amalgamation of a gold-leaf by mercury vapor with the phenomenon of deliquescence (p. 162).

8. If the scheme for the recognition of cations (p. 660) were applied to solutions prepared from materials containing (*a*) calcium oxalate and (*b*) potassium argenticyanide, at what stage and how would the presence of each of these substances affect the normal order ?

9. Why do none of the salts of the elements in this family give recognizable effects with the borax bead ?

CHAPTER XXXVIII

ELECTROMOTIVE CHEMISTRY

We have seen that chemical changes which proceed spontaneously liberate some form of energy. As a rule, heat is developed; but with special arrangement of the apparatus (p. 20) so that it takes the form of a battery-cell, an equivalent amount of electricity is obtained instead. To avoid suggesting that this energy comes from nothing, we say that the original system contained a certain amount of free, or available, chemical energy and that this has been transformed, concomitantly with the chemical change, into an equivalent amount of heat, or of electrical energy, as the case may be. Nor is the alternative of producing electrical energy available only when the action resembles the displacement of hydrogen by zinc, as in our illustration. Most changes between ionogens, including oxidations and double decompositions, may be adapted so as to deliver this form of energy. It need hardly be added that, since the transformation of chemically equivalent amounts of different sets of substances produces very different quantities of heat, so it produces also correspondingly different amounts of electrical energy. Thus the original free chemical energy may, theoretically, be measured by either method. In practice, however, the thermochemical plan fails entirely in many cases (*cf.* pp. 27, 79), and the electrical is, as we shall see, often much more instructive. The study of what, to parody the phraseology of thermochemistry, we might call "exoelectrical" actions, thus resolves itself into constructing experimental battery-cells involving all kinds of chemical changes, and studying the electric currents which are *set in motion* by the progress of the changes. We have therefore named this branch of the science **electromotive chemistry**.

In addition to its significance theoretically, electromotive chemistry has recently acquired great commercial importance because of the rapid multiplication of electro-chemical industries. It is true that the majority of the actions used in these industries are electrolytic (endoelectrical), and that this sort of change is the precise inverse of the other, since in it electricity is consumed instead of set in motion,

but it is also true that neither variety can be understood without a study of both.

Factors and Units of Electrical Energy. — On account of the close relation between electromotive chemistry and electrolysis, parts of the former subject were anticipated when the latter was discussed (pp. 321–325). These pages should now be re-read attentively. In particular, it must be recalled that a quantity of electrical *energy* is expressed by two factors. One is called the **quantity of electricity**, and is measured in *coulombs*. The other is called the **electromotive force** in the case of a current, or, when a current is not flowing or is not being considered, the **difference in potential**, and is expressed in *volts*. Just as in electrolysis chemically equivalent quantities of elements or ions, in being liberated from solutions of different substances, *use up* equal quantities of electricity (p. 317), so in a battery-cell the interaction of chemically equivalent amounts of different sets of substances *produces* equal quantities of electricity (p. 321). Likewise, just as in the former case different amounts of electrical energy (p. 323), and therefore different electromotive forces, are required to produce in different solutions equivalent amounts of chemical change (p. 324), so in the latter case different amounts of electrical energy are generated by the complete interaction of chemical equivalents of different sets of substances, and therefore diverse differences in potential are created and currents of *different electromotive force are produced.* The electrical energy used in the former case or produced in the latter is expressed by the product of the factors :

No. of coulombs × No. of volts = Quant. of elect. energy (in *joules*, p. 25).

If we consider the time occupied by either process, and wish to express the *rate* at which the energy is consumed or produced, we regard 1 coulomb per second (1 *ampere*) as the unit.
Hence :

No. of amperes × No. of volts = Rate of production or consumption of electrical energy (in joules per sec. = *watts*).

The erg (p. 25) is so small as a unit of energy or work, that the *joule* (= 10,000,000 ergs) and the *kilojoule* (1000 joules) are more often employed. Similarly, the rate at which the energy is delivered or used (the *power*) is expressed by the *watt* (= 10,000,000 ergs per sec.) or the *kilowatt* (1000 watts). The horse-power is 736 watts. Thus

the electrolysis of one formula-weight of hydrochloric acid (36.5 g.) requires 96,540 coulombs (p. 323) and an E.M.F. of 1.41 volts (p. 324). The electrical energy needed to perform this work is therefore 96,540 $\times$ 1.41 = 136,121 joules.

Displacement Cells. — While various kinds of chemical changes may be arranged to deliver electricity, we shall confine our attention almost entirely to actions in which one free substance displaces another from combination. Amongst the metals the order of displacing power is as follows (p. 362):

$$Mg - Zn - Cd - Fe - Sn - Pb - H - Cu - Hg - Ag - Pt - Au.$$

We have already noted many of the single facts expressed by this list. Thus, metallic copper precipitates metallic mercury, silver, platinum, and gold from solutions which contain salts of these elements, but it is in general entirely inactive in solutions containing salts of the elements which precede it in the list. Conversely, all the metals preceding copper will severally precipitate metallic copper from a solution of a cupric salt, but the metals following copper do not affect the solution at all. Furthermore, the speed with which the precipitation is effected and the amount of heat evolved are greater when copper precipitates gold than when it precipitates silver: they are also greater when magnesium precipitates copper than when tin does so. The same statements apply, *mutatis mutandis*, to each of the other elements. This is the behavior when the experiment is made in the ordinary way.

One preliminary condition is indispensable when electricity is to be obtained. When the zinc was placed in sulphuric acid and connected with a platinum wire (p. 20), there was nothing to prevent the metal from interacting directly with the acid, and generating heat. In fact, it did so act. Hydrogen appeared on the zinc itself, as well as on the platinum, and *both* the heat and the electricity would have had to be counted if a measurement or study of the relation between the amount of zinc and acid used and the quantity of energy produced had been in question. Since this is precisely the present problem, all the energy must now be secured as electricity, and the only way to accomplish this is *to prevent the mingling of the interacting materials.* Paradoxical as it may seem, it is easily possible to get the electricity and yet fulfil this essential condition. The plan in all battery-cells is to place the one substance in or around one pole, and the other substance

around or in the other pole, and to separate the substances by a porous wall or equivalent arrangement. The figure (Fig. 102) shows diagrammatically the plan that will serve for the generation of electricity by the use of any interaction.

Suppose the action is a displacement, and that, for example, the metal is zinc and the salt cupric sulphate in solution. The pole on the left is metallic zinc; the solution to the right of the porous partition contains the cupric sulphate. To complete the arrangement, a pole made of some conductor is needed on the right, and a conducting solution on the left. For these, any substances may be chosen, provided only that *they do not interact with the adjacent material.* If they do, part of the two main substances will be used up, with generation of heat instead of electricity. For the pole we may take copper itself or any metal *following* it in the series; and copper is less expensive than any of these. For the solution we may take a salt of zinc or of any metal *preceding* zinc in the series, provided that the salt chosen will not interact with the cupric sulphate which it meets inside the porous wall. Zinc sulphate or sodium chloride will serve the purpose. The function of the porous partition is to permit the migration of ions, but prevent a general mixing of the materials. It is evident that, when the corresponding conditions are observed, any other pair of elements from the series may be chosen for study. In practice, it is common to place the solution of the substance corresponding to the cupric sulphate along with its electrode in an outer jar, and a rod of the more active metal along with its conducting fluid in an inner jar made of porous earthenware. The following are the phenomena observed:

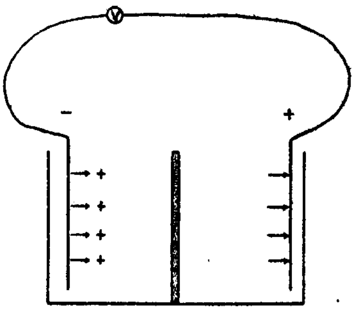


FIG. 102.

1. The pole on the left becomes charged negatively on account of the departure of positively charged ions from its surface, for this metal (zinc, for example) goes into solution. The pole on the right becomes positively charged on account of the discharge of positive ions, and deposition of the metal (copper, for example) on its surface. A current, therefore, flows from + to − through the wire, and passes in the form of migrating ions from − to + through the liquids. The negative

ions simultaneously drift away from the pole where the solution is losing metal, towards the pole where it is gaining metal, and so the balance of the two sorts of ions is preserved in every part of the liquids. The pole on the left is the anode, that on the right the cathode. This whole state of affairs continues until either all the copper is precipitated, or all the zinc is consumed.

2. The difference in potential (E.M.F.) is not affected by changes in the size or shape of the poles or in the amounts of the solutions, provided the materials are not changed. It is very noticeably affected, however, by alterations in the concentrations of the solutions. In particular, an increase in the concentration of the ions round the cathode (the $Cu^{\cdot\cdot}$ ions, for example) increases the difference in potential. It seems to assist the action by helping to force the ions out of the solution.

3. In general, the magnitude of the electromotive force is greater the farther the chosen metals are removed from one another in the series. Zinc with cupric sulphate gives a greater difference in potential than cadmium with the same salt, but a smaller one than zinc with silver nitrate. The sum of the differences in potential of the pairs $Zn–Cd^{\cdot\cdot}$, $Cd–Cu^{\cdot\cdot}$, $Cu–Ag^{\cdot}$, is exactly equal to the difference of the pair $Zn–Ag^{\cdot}$, provided solutions of equivalent ionic concentration are employed.

4. The quantity of electricity produced depends on the number of equivalents of material consumed. The strength of the current (the rate at which the electricity is developed) depends on the surface of the poles and other circumstances which influence the rate at which the materials are able to undergo chemical change. One gram-equivalent of the active metal (say, 32.7 g. of zinc) in becoming ionized will set in motion 96,540 coulombs, and deposit one gram-equivalent of the less active metal (say, 31.8 g. of copper). If this amount were to be ionized during every thirty minutes (= 1800 seconds) — and plates of great surface would be required to make this possible — the current strength would be 96,540/1800 = 53.6 amperes.

Potential Differences Produced by the Metals Singly. — The facts just discussed may be stated in various ways. For example, we may say that, since every metal (save the last of the series) displaces some other metal or metals, each metal has a distinct tendency to become ionic. We may picture this as a pressure or tension driving the particles into solution, and actually resulting in ionization when the necessary electricity is available. This pressure must evidently

be greatest with magnesium, and least with gold. On the other hand, we may suppose a converse tendency of the ions to force themselves out of solution and to deposit themselves on the cathode, this tendency actually becoming continuously operative when means of disposing of the electric charges is provided. This tendency is evidently greatest with gold, and least with magnesium. Now the use of cells like those described above does not enable us to verify these hypotheses, because in each cell two operations are going on simultaneously, and the electrical effects are the joint result of both. Fortunately it has been found possible to observe and measure the electrical effects at each end of the cell separately. It is found, in fact, that the difference in potential between the poles is for the most part made up of the differences in potential between each pole and the liquid in which it is immersed.

After the cell has been in operation for some time, the cathode system consists of a pole covered with deposited metal (say copper) in contact with a solution containing ions of this same element. At this end the ions are diminishing in number, and the amount of free metal is increasing. The anode system likewise consists of a metal (say zinc) in contact with a solution containing ions of the same element. Here the number of ions is increasing, and the metal is wearing away. The ions of the foreign salt, if such a salt was introduced at first, need not be considered. Thus, for the purpose of making a strict comparison, we may immerse each metal of the series in a solution of one of its own salts, taking the latter of such strength that there is normal concentration of the metallion, and measure the difference in potential between the metal and the solution.

The following table (p. 670) contains data obtained in just this way. The number opposite each of the twenty-six metals (including hydrogen) represents the potential difference. The sign preceding the number indicates the nature of the electrical charge borne by the *solution*.

Two or three examples will make the meaning of the table clearer. Opposite Mg, we find + 1.21. This means that when the metal magnesium is immersed in a solution of a magnesium salt containing a normal concentration of $Mg^{\cdot\cdot}$, the solution becomes positively charged (the metal, negatively) and that the difference in potential between metal and solution is 1.21 volts. Similarly in the case of zinc, the solution is positive, but the potential difference is smaller. With copper the solution is negative (and the metal positive). With silver the solution is negative, and more strongly so than with copper. Cobalt

is near the border line, the normal solution of cobaltion being very slightly negative.

POTENTIAL DIFFERENCES IN VOLTS FOR NORMAL SOLUTIONS OF CATIONS.

K	(+ 2.9)	Ni	– 0.04
Na	(+ 2.54)	Sn ($Sn^{\cdot\cdot}$)	– 0.08 ?
Ba	(+ 2.54)	Pb	– 0.13
Sr	(+ 2.49)	H	– 0.28
Ca	(+ 2.28)	Cu ($Cu^{\cdot\cdot}$)	– 0.61
Mg	+ 1.21	As	– 0.62 ?
Al	+ 1.00	Bi	– 0.67 ?
Mn	+ 0.80	Sb	– 0.74 ?
Zn	+ 0.49	Hg ($Hg^{\cdot\cdot}$)	– 1.03
Cd	+ 0.14	Ag	– 1.05
Fe ($Fe^{\cdot\cdot}$)	+ 0.06	Pd	– 1.07 ?
Tl	+ 0.04	Pt	– 1.14 ?
Co	– 0.04	Au	– 1.35 ?

For a hydrogen pole a piece of palladium saturated with hydrogen gas is used. The values for the metals which decompose water with ease cannot be ascertained by direct observation. The numbers in parentheses are calculated from the heats of ionization and serve simply to indicate the order of these elements. An interrogation point indicates that the value is uncertain.

These facts enable us to state in more definite terms the formulative hypothesis foreshadowed above. It was first put forward by Nernst.

Every metal has a certain **solution tension** or pressure tending to drive it into solution (in ionic form,* of course, since it is not soluble otherwise). The value of this pressure becomes rapidly less as we pass through the series from magnesium to gold. If the ions of the same metal are already present, they tend to give up their electrical charges and deposit themselves upon the metal. These two tendencies oppose one another just as solution pressure and osmotic pressure oppose one another in the ordinary process

* The idea of the charge of electricity is apt to interfere with the ready acceptance of this hypothesis. If it is remembered that the ionic form of an element is simply an allotropic modification (Ostwald) with a different amount of available energy, the difficulty disappears. In the ionic allotrope the free energy is sometimes greater (cobalt to platinum) and sometimes less (potassium to thallium) than in the free element.

of dissolving any substance (p. 152). When the tendency of the ions to deposit themselves is the greater of the two, a very minute excess of deposition over solution occurs, and thus the solution has, as a whole, a negative charge (having lost some positive ions), and the metal has a positive charge (having acquired it from the deposit of a few ions). This is the case with gold and the metals as far up the list as cobalt. When, on the other hand, the solution pressure of the metal is the greater of the two, the solution acquires a very slight excess of positive ions, and is, therefore, positively charged when compared with the metal. This is the case from potassium down to thallium.

The measure of the "tendency of the ions to deposit themselves" is simply the osmotic pressure of the metallions. We perceive this to be the case, for, when we take a stronger solution of the salt and therefore an increased osmotic pressure of the ions, an instant effect is produced. The solution becomes less positive, or more negative, as the case may be. Evidently the solution pressure of each of the metals near to cobalt is almost exactly balanced by the osmotic pressure of a normal solution of the ions composed of the same metal. This pressure, for a univalent metal, is 22.4 atmospheres (p. 289), and for a bivalent metal 11.2 atmospheres. The metals above cobalt have solution pressures higher and higher above this norm; those below cobalt have solution pressures farther and farther below it. The effect of changing the osmotic pressure is independent of the particular substances used, and depends only on the valence. When the concentration of the metallion becomes $10N$, 0.058 volts must be subtracted (algebraically) from the potential (see above table) of the liquid, if the metallion is univalent. If it is n-valent, $0.058/n$ must be subtracted. When the solution is 0.1 N, $0.058/n$ volt must be added; when it is 0.01 N, $2 \times 0.058/n$ must be added, and so forth. Thus, zinc with deci-normal zincion gives $+ 0.49 + 0.058/2 = .52$ volts, approximately; silver with centinormal argention gives $-1.05 + (2 \times 0.058) = -.93$ volts, approximately. And, in general, if c be the equivalent concentration of the metallion in the liquid under consideration, and π_c the electrical potential of that liquid, while π_N is the potential of the liquid containing N metallion,

$$\pi_c = \pi_N + \frac{0.058}{n} \log \frac{1}{c}.$$

Application to Cells. — When, now, a cell with *two* poles and *two* metallions is set up, we can tell from the above table what the differ-

ence in potential between the two poles will be. We may regard the two systems—the anodic and cathodic—as working against each other. Each metal tends to project its ions into the solution and to generate a positive current in the liquid and a negative one in the wire. If both solutions are normal, or, in general, of equal equivalent concentration, the relative solution pressures of the metals decide the direction of the resultant current, and its magnitude will be the *difference* of the two effects. Thus, the values for the following pairs will be:

Zn–Cd••, $+0.49-(+0.14)=+0.35$, Zinc the negative pole.
Cd–Cu••, $+0.14-(-0.61)=+0.75$, Cadmium the negative pole.
Zn–Cu••, $+0.49-(-0.61)=+1.1$, Zinc the negative pole.

The Daniell or gravity cell (Fig. 103) represents the last of these three combinations. The copper pole is at the bottom, and the zinc plate is suspended above it. The cell is charged with a dilute solution of sodium chloride, and blue vitriol crystals are thrown in and dissolve. So long as the contents are not disturbed, the solutions require no porous septum to keep them apart. It is true that, when the current is not being used, and the cell is not working, the cupric sulphate diffuses upwards. During the time that the circuit is closed, however, the effects of diffusion are nullified by the migration of the cuprion away from the zinc and towards the positive pole. The actual electromotive force of the current delivered by this cell is a little over 1 volt, and accords, therefore, with the value calculated from the potential difference observed at each of the two poles.

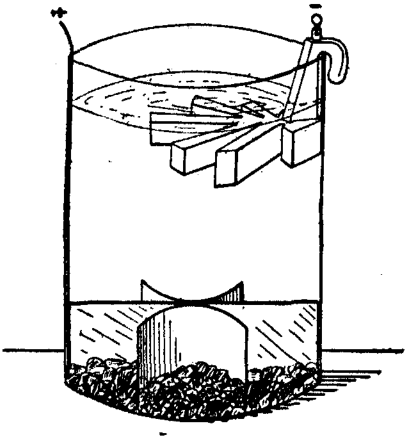


FIG. 103.

The cell Zn–H• (0.77 volts) works without a septum, provided the direct action of the zinc on the acid is minimized by adequate amalgamation with mercury. It gives a very inconstant electromotive force, however, because the platinum plate used as the cathode becomes covered with bubbles of hydrogen, and so the internal resistance of the cell

is greatly increased. The polarization (p. 324) also diminishes the electromotive force. These difficulties are remedied, and, in fact, a great increase in the E.M.F. of the cell is effected, by surrounding the cathode with an oxidizing agent which shall convert the hydrogen into water. The energy obtainable is thus that of a strong oxidizing agent on zinc, and not merely that of an acid. In the **Bunsen cell** the cathode is a carbon block surrounded by concentrated nitric acid. In the **dichromate battery** it is a carbon block with chromic acid. Each of these cells gives an E.M.F. of 1.9 volts. In the **Leolanché cell** the cathode is a mixture of carbon and manganese dioxide, and the fluid is a solution of ammonium chloride from which the zinc displaces hydrogen. The dioxide, being solid, oxidizes the hydrogen slowly, and the cell can be used for only a few minutes at a time without becoming polarized. The E.M.F. is 1.48 volts. **Dry cells** are of the same nature, but contain a porous solid which holds the liquid by capillary forces (for Accumulators, see under Lead).

A cell is thus an engine for the direct transformation of chemical into electrical energy, just as a steam-engine transforms chemical energy, by several stages, it is true, into mechanical energy. According to our hypothesis the cell is driven by pressure-differences in the materials in and around the two poles.

Other Applications: Couples: Concentration Cells. — We are now in a position to understand the effect of a **couple** (p. 96). Zinc, in contact with platinum or copper and immersed in acid, is practically a short-circuited cell, and it is found that, for some undetermined reason, hydrogen is liberated more readily from the surface of the platinum or copper than from that of the zinc. Again, galvanized iron is also a couple. The zinc is the anode, and, when dilute carbonic acid rests on a damaged part of the surface of a sheet of the material, and is in contact with both metals, the zinc is ionized and passes into combination as carbonate. The iron is the cathode and is not affected. On the other hand, a damaged tin-plate (tin on iron) is rapidly rusted. Here iron is the anode, and goes into combination, while the tin is the cathode. The ferrous carbonate (*q.v.*), at first formed, is subsequently oxidized and gives rust.

When two strips of a metal are immersed together in a solution of a salt of the same metallic element, — for example, two rods of tin in a normal solution of stannous chloride, — the pieces of metal show no difference in potential and no current flows when they are connected

by a wire. The two poles and their solutions are here alike and $-.07-(-.07) = 0$.* But if the solution round one pole is diluted to $N/10$ concentration, the potential at that pole becomes at once $-.07 + .058/2 = -.04$ volts, approximately, and a current is set up. The positive current flows from the pole in the stronger solution through the wire to that in the dilute solution, and thence through the liquid. Thus, tin is dissolved from the latter pole (the anode), and the concentration of the solution round it is increased. On the other hand, tin is deposited in long needles on the former pole (the cathode), and the concentration in its neighborhood is correspondingly decreased. The figure (Fig. 104) shows the simplest arrangement, where the more concentrated, denser liquid is below, and one rod of tin, passing through both layers, furnishes at once the two poles and the connection. The chloridion migrates through the solution, in a direction opposite to that taken by the tin ions, and thus passes upwards into the dilute solution to balance the fresh tin ions that are continuously formed. All change ceases when the concentrations have become equalized. A cell of this kind is called a **concentration cell.**

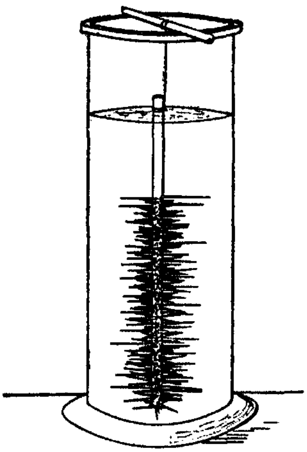


FIG. 104.

The concentration cell is instructive because it shows that the order of the metals in the electromotive series is not determined by the metal alone, but also by the concentration of the solution. The order of the metals in the electromotive series is therefore subject to variation. An extreme case of this occurred in a recent chapter. Zinc displaces copper from a solution of a cupric (or cuprous) salt, and any but a prodigiously dilute solution will show the effect. But a solution containing cuprocyanion $Cu(CN)_2'$ has precisely this very minute concentration of copper ions which will turn the scale. Hence, zinc will not displace copper from this solution (p. 624). On the contrary, copper will displace zinc from a solution of a salt of the latter containing excess of potassium cyanide, and therefore the complex salt $K_2Zn(CN)_4$.

* In copper refining (p. 617), the state of equilibrium is destroyed and the scale turned by the introduction of a current of low E.M.F. from a dynamo.

The **solubilities of insoluble salts**, such as those of silver (p. 630), **have** also **been measured** on the principle of the above tin cell. If a saturated solution of silver chloride is placed round one pole of silver, and normal argention (say from silver nitrate) round another, a concentration cell of high E.M.F. is formed. The magnitude of the difference in potential enables us at once to calculate the ratio of the concentrations of argention round each pole, and therefore to get at the concentration of the silver chloride solution.

Electrolysis : Discharging Potentials. — Another kind of cell may be made by placing a rod of tin (or any other metal) in an electrolyte on one side of a porous septum (say on the left side of the cell shown in Fig. 102), and chlorine water on the other. An indifferent ionogen (say KCl) must be used on the right side also, because chlorine water is not a good conductor. A platinum plate is likewise required as a pole at this end. With this arrangement the tin becomes ionized and renders its pole negative. Simultaneously the chlorine in contact with the platinum becomes ionic and leaves the other pole positive. Thus, a current of considerable E.M.F. flows from the platinum pole to the tin pole through the wire. Tin ions and chlorine ions are formed, and therefore, potentially, tin chloride. But it will be noted again that the materials have to be kept apart, otherwise direct union and mere heat-production will result.

Now it will be recalled (p. 324) that when a salt is electrolyzed, the materials liberated on the electrodes generate a counter current, called the **polarization current**, which it is the business of the electrolyzing current to overcome. It will now be clear that the cell just described is identical with the arrangement which would result from electrolyzing tin chloride. The amount by which the E.M.F. of the electrolyzing current is cut down (p. 324) by the polarization current is exactly equal to the potential of a cell like the above containing the same elements. The minimum difference in potential which will decompose an electrolyte is called the **discharging potential** and is numerically equal to the E.M.F. of the corresponding battery-cell, but of opposite sign. Furthermore, since the potential of a cell is made up of two simple potentials, the discharging potential must be made up of the same two (discharging) potentials. Thus, with the help of a list of anions and their single potentials, we can calculate at once the total E.M.F. required to electrolyze any salt. A few of the values are as follows:

POTENTIAL DIFFERENCES FOR ANIONS (IN VOLTS).

I	– 0.80	OH	– 1.96
Br	– 1.27	SO_4	– 2.2
O	– 1.36	HSO_4	– 2.9
Cl	– 1.69		

As before, the anode potential is supposed to work against the cathode potential and is subtracted from it. Thus, the tin-chlorine cell produces $-0.08-(-1.69)=1.61$ volts, and this E.M.F. will just suffice to electrolyze tin chloride. Similarly, hydrochloric acid will require at least $-0.28-(-1.69)=1.41$ volts, zinc sulphate $0.49-(-2.2)=2.69$ volts.

Oxygen acids like sulphuric acid show a trace of decomposition at 1.08 volts ($=-0.28-(-1.36)$), and a noticeable but still small decomposition at 1.68 volts ($=-0.28-(-1.96)$), due to the $H^{\bullet}$ and O'' and the $H^{\bullet}$ and OH' respectively. But it is only when the E.M.F. reaches the values for $H^{\bullet}$ and SO_4'', and $H^{\bullet}$ and HSO_4', namely, 1.92 and 2.62 volts, that rapid electrolysis begins. This observation answers, incidentally, the question whether in the so-called "electrolysis of water," when dilute sulphuric acid is used, it is the water or the acid that is decomposed. The $H^{\bullet}$ and OH' decomposition at 1.68 volts is very slight, because of the small concentration of the OH', and a lens is required for its recognition. The more vigorous action resulting from the discharge of SO_4'' and HSO_4' by the use of 2–3 volts is therefore the one invariably used.

In view of the foregoing facts, it is probably most correct to say that when dilute sulphuric acid is electrolyzed, *e.g.* as a lecture experiment, the oxygen liberated at the anode comes mainly from a secondary interaction of the discharged material of the anions with the water (p. 95). A minute proportion of the oxygen in such an experiment does arise from primary electrolysis of the water, but this effect of the current is in itself too slight to be visible at a distance. When, on the other hand, the solution electrolyzed contains a salt of sodium, and hydrogen is liberated at the cathode, this gas must probably be regarded as coming chiefly from primary electrolysis of the water. The discharging potential for sodium chloride should be $+2.54-(-1.69)=4.23$ volts, and with the help of a mercury cathode a sodium amalgam is easily obtained (p. 554). But it will be found that, with platinum electrodes, hydrogen and chlorine are liberated freely from a solution of salt by a current of little more than half the above mentioned E.M.F. The positive electricity is carried in the

liquid mainly by the very numerous sodium ions. But, apparently, when these ions reach the cathode, the potential difference, being insufficient to discharge the natrion, liberates the hydrion of the water instead. Thus the accumulating hydroxidion of the water, and the natrion arriving by migration, together constitute the sodium hydroxide which is another product of this electrolysis. With higher E.M.F. and sufficient current density, natrion is doubtless actually discharged, and in that case a part of the hydrogen liberated is furnished by the interaction of the metal with the water.

The ordinary chemical behavior of the halogens accords with the order of their potential differences. Bromine displaces iodine, and chlorine displaces both (p. 361). Chlorine, however, does not displace easily perceptible amounts of oxygen from water, because of the small concentration of the O'' (obtained by secondary ionization of the OH'). The oxygen freely liberated in sunlight comes from the decomposition of the HClO (p. 269). Fluorine, however, which would probably show a potential difference below that of the much more plentiful OH', displaces oxygen vigorously by discharging this ion.

In electrolyzing a mixed solution with a moderate current, the cations and anions with the lowest discharging potentials are first liberated. Thus, silver (– 1.05) appears before copper (– 0.6). Hence, in copper refining (p. 617), the copper, of which there is a continuous supply, is deposited, and the more active metals remain combined. Indeed, the E.M.F. used is not sufficient in any case to discharge them.

The Factors of Energy.—We have seen that the amount of a given supply of electrical energy is described by two factors, the E.M.F. and the quantity of electricity, and that the weight of material, which, by its influence, undergoes a given chemical change, is proportional solely to this second factor. On the other hand, the question whether the supply of energy can *initiate the change at all* depends on the magnitude of the first factor alone (p. 324). The total amount of available energy does not influence the result if the E.M.F. is not above a certain minimum, which differs from case to case. Now the same is true of other kinds of energy. The quantity of each may be expressed as the product of an **intensity** factor and a **capacity** factor. The magnitude of the former determines whether the energy can be transferred or transformed or not. Heat energy, no matter how much of it is at hand, can neither flow nor be transformed into work unless the

source is at a higher **temperature** than the surroundings. A head of water will do work only when it is connected with a receptacle at a lower level. It is the **pressure** of the water that determines its availability. The E.M.F. is the corresponding factor of electrical energy.

Now we may presume that chemical energy can be expressed by two factors. One of these, the capacity factor, must be proportional to the quantity of material, in other words, to the number of chemical equivalents. The other is the **chemical potential**. A chemical change which does not take place on a small scale will not take place when more material is used, provided the relative amounts of the interacting substances and the conditions remain unchanged.* We have, in fact, been assuming all along that this, the capacity factor, is not the most significant one. But we have devoted ourselves to noting such things as these: that chlorine will displace bromine, and therefore has the higher potential of chemical energy; that magnesium reduces sand, while hydrogen does not, and that magnesium is therefore a more active reducing agent; and that hypochlorous acid will oxidize indigo, while free oxygen will not, and is therefore a more powerful oxidizing agent. When we were comparing degrees of **activity**, therefore, we were really trying to describe the relative potential of the chemical energy in all sorts of substances. At present the state of the science permits this to be done in most cases in a rough fashion only.

Since the capacity factor of chemical energy is proportional to the number of equivalent weights transformed, and the capacity factor of electrical energy is proportional to the same thing (Faraday's law), it follows that the intensity factor of the chemical energy (the chemical potential) in a given substance undergoing a given change, must be proportional to the corresponding factor (the E.M.F.) of the electrical energy produced when the same change takes place in a suitable cell. The potential differences described above are therefore often much more significant than are the results of thermochemical measurements, for the latter attempt to give only the gross quantity of chemical energy (in terms of the equivalent amount of heat energy), and not the values of the factors. The potential differences come nearer, therefore, to giving us absolute values for chemical activity than do any other data we possess.

As we have noted before (p. 78), in spite of the enormous range of temperature at our disposal, extending to a point far above 2500° in

* Change in concentration, however, does affect activity, and therefore modifies the chemical potential.

the electric furnace, there are many substances for whose decomposition a sufficient potential of heat energy is not available. On the other hand, amongst substances that are capable of furnishing an electrolyte, when dissolved in a suitable solvent or when fused, there are few that are not decomposable by a current with an E.M.F. of less than 10 volts. Hence even the elements which give the most stable compounds and are the most difficult to isolate, such as calcium and aluminium, are liberated by electrical methods with extreme ease.

Methods of Measuring Chemical Activity. — The following is a summary of the methods of measuring chemical activity.

The **thermochemical method** (p. 79) can be used in every chemical change. But the heats of reaction represent the free energy, and therefore the affinity, only when the heat capacity of the products is equal to that of the factors and no changes in concentration arise.

For measuring the **activity of acids** in dilute solution, several methods have been mentioned: The speed of interaction of different acids with the same metal (p. 347); the acceleration of the speed of hydrolysis of ethyl acetate (p. 504) and of cane-sugar (p. 500) by different acids; the amounts of insoluble salts, such as calcium oxalate (p. 598), or zinc sulphide, which, when the system has reached equilibrium, are found to have been decomposed by different acids under like conditions; the relative extents of the hydrolysis of salts of different weak acids (p. 344); the electrical conductivity (p. 325) and the freezing- and boiling-points of solutions of acids (pp. 292, 293). These last measure by physical methods the same thing that the others determine by chemical means, namely, the tendency to ionization on which the activity of acids depends (p. 347. See also p. 356).

For measuring the **activity of bases**, we have: The relative speeds of saponification of esters by different bases (p. 505); the relative extents of the hydrolysis of salts of different weak bases (p. 344); the conductivity and the freezing- and boiling-point methods, which measure by physical means the tendency to ionization.

For measuring the relative **activities of metals** and **non-metals**, we have: The single potential differences (pp. 670, 676); and, for the former, the speed of interaction of different metals with the same acid (p. 111).

For measuring the relative **activity in non-reversible actions**, we have: The speed with which the actions take place under like conditions (p. 250).

For measuring the relative **activities of the opposed actions in reversible changes**, we have: The concentrations of the materials remaining when equilibrium has been reached (p. 254). The relative activities in **different reversible changes** may also be ascertained by comparing the concentrations in one, at equilibrium, with those in another (*cf.* p. 257).

For measuring the relative **activities of oxidizing** and **reducing agents**, we have: The potential differences in cells arranged after the manner of the Bunsen and Leclanché cells (p. 673).

If we consider the whole mass of phenomena, it must be admitted that the scientific study of the quantities of material has reached a far higher level of exactness, and has very much more nearly enveloped the whole field covered by the science, than has the study of relative activity. Yet it is evident that within the past few years substantial advances have been made in this direction also.

Exercises. — 1. What will be the E.M.F. of each of the following cells when each of the metallions is present in normal concentration: Mn — $Cu^{\cdot\cdot}$, Cd — $Pb^{\cdot\cdot}$?

2. What will be the E.M.F. of a concentration cell in which the poles are of lead and the plumbion is one hundred times more concentrated round one pole than round the other?

3. What will be the discharging potential for solutions of the following substances, if we assume that the concentration of the ions is normal: manganous chloride, hydrogen bromide?

4. What weight of aluminium must become ionized every hour in a cell in order that a current of five amperes strength may be produced? What would be the E.M.F. of the current if an acid with normal concentration of hydrion surrounded the cathode and a solution of normal aluminion the anode? How would this E.M.F. be affected if the aluminion was only one-hundredth normal?

CHAPTER XXXIX

ALUMINIUM AND THE METALS OF THE EARTHS

THE fourth column of the periodic table (p. 411) contains boron and aluminium along with a number of rare elements. The chief members of the family are: boron (B, at. wt. 11), aluminium (Al, at. wt. 27.1), gallium (Ga, at. wt. 70), indium (In, at. wt. 115), thallium (Tl, at. wt. 204.1), all on the right side of the column, and scandium (Sc, at. wt. 44.1), yttrium (Yt, at. wt. 89), lanthanum (La, at. wt. 138.9), samarium (Sa, at. wt. 150.3), and ytterbium (Yb, at. wt. 173) on the left side. These elements are all trivalent.

The Rare Elements of this Family. — The oxide and hydroxide of boron are acidic (p. 527). Those of aluminium ($Al(OH)_3$), gallium ($Ga(OH)_3$), indium ($In(OH)_3$), and thallium ($TlO.OH$) are basic, but behave also as acids towards strong bases.

Gallium and **indium** occur occasionally in zinc-blende, and were discovered by the use of the spectroscope. The former takes its name from the country (France) in which the discovery was made, and the latter from two blue lines shown by its spectrum. Indium gives a complete series of compounds in which it is trivalent, and the chlorides $InCl$ and $InCl_2$ are also known.

Thallium is found in some specimens of pyrite and blende. It was discovered by Crookes by means of the spectroscope in the seleniferous deposit from the flues of a sulphuric acid factory. It received its name from the prominent green line in its spectrum (Gk. θαλλός, a green twig). It gives two complete series of compounds. In those in which it is trivalent (thallic salts), it resembles aluminium (*q.v.*). Thus, the salts of this series are more or less hydrolyzed by water. Univalent thallium recalls both sodium and silver. Thallous hydroxide ($TlOH$) is soluble, and gives a strongly alkaline solution. The chloride is insoluble in cold water. The solutions of the thallous salts are neutral. The metal is displaced from its salts by zinc.

Of the elements on the left side of the column, **scandium**, whose existence and properties were predicted by Mendelejeff (p. 412), is the

best known. The metals of the **rare earths**, of which it is one, are found in rare minerals such as euxenite, gadolinite, orthite, and monazite, which occur in Sweden, Greenland, and the United States. **Cerium** (Ce, at. wt. 140.25), **neodymium** (Nd, at. wt. 143.6), and **praseodymium** (Pr, at. wt. 140.5), occur along with **lanthanum** in cerite, a silicate of these four elements. These four are included amongst the metals of the rare earths. The compounds of many of these rare elements behave so much alike that separation is difficult. It is certain, however, that there are several with atomic weights near to that of lanthanum for which accommodation cannot easily be found in the periodic table, and some of these are probably mixtures of still more closely related elements. Ostwald has compared them to a group of minor planets such as in the solar system takes the place of one large planet.

ALUMINIUM.

The Chemical Relations of the Element. — Aluminium is trivalent exclusively. Its hydroxide, like that of zinc (p. 648), is feebly acidic as well as basic, and hence the metal forms two sets of compounds of the types $Na_3.AlO_3$ and $Al_2.(SO_4)_3$. The salts of both series are more or less hydrolyzed by water, the former very conspicuously so. It is worth noting that the hydroxides of the trivalent metals, or metals in the trivalent condition, such as $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, are all distinctly less basic than are those of the bivalent metals such as $Zn(OH)_2$, $Cd(OH)_2$, $Fe(OH)_2$, $Mn(OH)_2$. This fact is used in analysis (*cf.* also p. 661) in separating the two sets. When a solution of the chlorides is shaken with precipitated barium carbonate, the free acid from the more highly hydrolyzed salts of $Al^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ interacts with this substance, the hydrolysis is promoted:

$$AlCl_3 + 3H_2O \rightleftarrows Al(OH)_3 + 3HCl,$$

and eventually the hydroxides $Al(OH)_3$, $Cr(OH)_3$, and $Fe(OH)_3$ are completely precipitated. The chlorides of the bivalent metals remain in the solution. Aluminium does not enter into complex anions or cations, and is too feebly base-forming to give salts like the carbonate or sulphite.

Occurrence. — Aluminium is found very plentifully in combination, coming next to oxygen and silicon in this respect. The feldspars (such as $KAlSi_3O_8$), the micas (such as $KAlSiO_4$), and kaolin (clay

$H_2Al_2(SiO_4)_2,H_2O$), are the commonest minerals containing it. Garnets, which are found in metamorphic rocks, are mainly an orthosilicate of calcium and aluminium $Ca_3Al_2(SiO_4)_3$. Turquoise is a hydrated phosphate $Al_2(OH)_3PO_4,H_2O$, and cryolite a double fluoride $3NaF,AlF_3$. Various forms of the oxide and hydroxide (see below) are also not uncommon minerals.

Preparation and Physical Properties. — The metal is now made on a large scale by electrolysis of the oxide (Al_2O_3) dissolved in a bath of molten cryolite. The operation is conducted in cells, the carbon linings of which form the cathodes. The anodes are rods of carbon which combine with the oxygen as it is liberated. The metal sinks to the bottom of the cell and is drawn off periodically, while fresh portions of the oxide are added from time to time. A current density of 5 amperes per sq. cm. of cathode area and an E.M.F. of 5–6 volts maintain the temperature of the molten materials, and cause the decomposition.

The metal melts at 600–700°, but is not mobile enough to make castings. It is exceedingly light (sp. gr. 2.6), and in hardness and tensile strength is the equal of any of the other metals, with the exception of steel. It has a silvery luster, and does not tarnish, the firmly adhering film of oxide first formed protecting its surface. Although, comparing cross-sections, it is not so good a conductor of electricity as is copper, yet *weight for weight* it conducts better. It is difficult to work on the lathe or to polish, because it sticks to the tools, but the alloy with magnesium (6–30 per cent) called **magnalium** has admirable qualities in these respects. **Aluminium bronze** (5–12 per cent aluminium) is easily fusible, has a magnificent golden luster, and possesses mechanical and chemical resistance exceeding that of any other bronze.

The metal and its alloys are used for making cameras, opera-glasses, cooking utensils, and other articles requiring lightness and strength. The powdered metal, mixed with oil, is used in making a silvery paint.

Chemical Properties. — The metal displaces hydrogen from hydrochloric acid very easily. In sulphuric and nitric acid, however, it receives a coating of the hydroxide, formed by hydrolysis of the salt, and the action is slow in the former case, and almost nil in

the latter. It displaces hydrogen also from boiling solutions of the alkalies, forming aluminates:

$$2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2.$$

In consequence of its very great affinity for oxygen, aluminium displaces all the metals, save magnesium, from their oxides. Thus, when a mixture of aluminium powder and ferric oxide is placed in a crucible and ignited by means of a piece of burning magnesium ribbon, aluminium oxide and iron are formed:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe.$$

The very high temperature (about 3000°) produced by the action is sufficient to melt both the iron (m.-p. 1700°) and the oxide of aluminium. The products, not being miscible, separate into two layers. This very simple method of making pure specimens of metals like chromium, uranium, and manganese, whose oxides are otherwise hard to reduce, is called by Goldschmidt, the inventor, "aluminothermy." The sulphides, such as pyrite, are reduced with equal vigor by aluminium.

Aluminium Chloride. — If the metal or the hydroxide is treated with hydrochloric acid, and the solution is allowed to evaporate, crystals of $AlCl_3,6H_2O$ are formed. When heated, this hydrate is completely hydrolyzed, hydrochloric acid is given off, and only the oxide remains. The anhydrous chloride is much used as a catalytic agent for causing combination in organic chemistry. It is made by passing dry chlorine over aluminium, or by heating the oxide with carbon in a stream of chlorine. Just as in the case of silicon dioxide (p. 520), neither carbon nor chlorine alone will act upon the oxide.

Aluminium chloride gives a vapor pressure of 760 mm. at 183°, and sublimes, as a white crystalline solid, without melting. Under pressure, it melts at 193°. In the mode of preparation described above, it is, therefore, vaporized, and condenses in a cool part of the tube. It fumes when exposed to moist air on account of the hydrogen chloride produced by hydrolysis, and only with excess of hydrochloric acid does it give a clear solution free from basic salts.

Aluminium Hydroxide and the Aluminates. — When an alkali is added to a solution of a salt of aluminium, the hydroxide $Al(OH)_3$ is precipitated in gelatinous form. It is a white hydrogele (p. 523), and loses water gradually when dried, without forming any intermediate hydroxides, until Al_2O_3 alone remains. It interacts both with acids

and with bases, and is, therefore, like zinc hydroxide (p. 648), ionized both as a base and as an acid. It interacts only slightly with ammonium hydroxide, because this substance is too feebly basic, but, from the solution in the active alkalies, the aluminates $Na_3.AlO_3$, $Na.AlO_2$, and $K.AlO_2$, can be obtained in solid form. Natural forms of this substance are hydrargyllite $Al(OH)_3$ ($= Al_2O_3, 3H_2O$), bauxite $Al_2O(OH)_4$ ($= Al_2O_3, 2H_2O$), which always contains ferric oxide, and diaspore $AlO.OH$ ($= Al_2O_3, H_2O$).

Commercially, the hydroxide is made by heating bauxite with sodium carbonate. The ferric oxide, having no tendency to form a carbonate or to interact with a base, remains unchanged. The sodium aluminate which is formed can be extracted with water:

$$Al_2O(OH)_4 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2 + 2H_2O.$$

The hydroxide is then precipitated by passing carbon dioxide through the solution:

$$2NaAlO_2 + CO_2 + 3H_2O \rightarrow Na_2CO_3 + 2Al(OH)_3.$$

The aluminates are largely hydrolyzed by water:

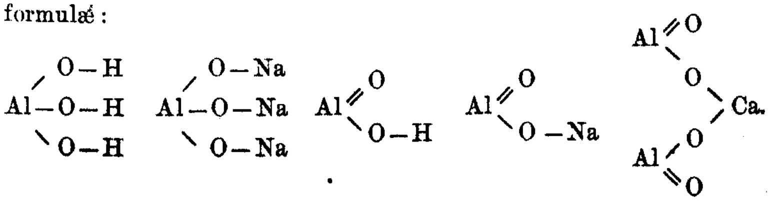
$$NaAlO_2 + 2H_2O \rightleftarrows NaOH + Al(OH)_3.$$

Hence an excess of sodium hydroxide is required for the complete solution of aluminium hydroxide by the reversal of this action. Sodium aluminate is used as a mordant in dyeing (see below), on account of the ease with which the solution gives up aluminium hydroxide when any material is present which can combine with the free portion of the hydroxide and so cause forward displacement of the above equilibrium.

When calcium chloride is added to a solution of sodium aluminate, the insoluble calcium metaluminate is deposited:

$$2NaAlO_2 + CaCl_2 \rightarrow Ca(AlO_2)_2 + 2NaCl.$$

The relations of these various substances are shown by the following formulæ:



A number of insoluble metaluminates are found in nature. They crystallize in the regular system, and are known as spinelles. They contain bivalent metals in place of the calcium in the last-named compound. Thus we have spinelle proper $Mg(AlO_2)_2$, and gahnite $Zn(AlO_2)_2$. Corresponding and isomorphous derivatives of chromic and ferric hydroxides are chromite $Fe(CrO_2)_2$ and magnetite $Fe(FeO_2)_2$.

Aluminium Oxide. — The oxide (**alumina**) is found in nature in pure form as corundum. This mineral is only one degree less hard than the diamond. Emery is a common variety, contaminated with ferric oxide, and is widely used as an abrasive. The ruby is pure aluminium oxide tinted by a trace of a compound of chromium, while the sapphire is the same material colored with aluminate of cobalt. Both can be made artificially by adding a little of the oxide of chromium or of cobalt when aluminium oxide is produced by Goldschmidt's method (p. 684). The alumina made by gently heating the hydroxide interacts easily with acids, but after being strongly heated it resembles natural alumina in being very slowly affected by them. Minerals containing insoluble compounds of aluminium are attacked when heated strongly with potassium bisulphate (*cf.* p. 560), the sulphate of aluminium being formed.

Aluminium Sulphate : The Alums. — The sulphate is prepared by treating either the hydroxide or pure clay (kaolin) with sulphuric acid. In the latter case the insoluble residue of silicic acid is removed by filtration:

$$H_2Al_2(SiO_4)_2 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 2H_2SiO_3 + 2H_2O.$$

The salt crystallizes from water as $Al_2(SO_4)_3, 18H_2O$, forming aggregates of leaflets which are very soluble. The solution is acid in reaction. This compound is used as a mordant under the name of "concentrated alum." It is employed also in **sizing** cheaper grades of **paper**, an operation required to prevent the absorption and consequent spreading of the ink. For writing-paper, gelatine solution is employed. In making printing-papers, rosin soap (made by dissolving rosin in caustic soda) is mixed with the pulp, and aluminium sulphate is added. The rosin and aluminium hydroxide are precipitated, perhaps in feeble combination, and pressing between hot rollers afterwards melts the former and gives a surface to the paper.

When sulphate of potassium is added to a strong solution of alu-

minium sulphate, octahedral crystals of alum (potash alum, $K_2SO_4, Al_2(SO_4)_3, 24H_2O$) are deposited. This is a double salt, and is one of a large number known as the **alums**. These have the general formula $M_2^ISO_4, M_2^{III}(SO_4)_3, 24H_2O$, and may be made as above by using a sulphate of a univalent metal with one of a trivalent metal. Thus, for M^I we may use K, NH_4, Rb, Cs, and Tl^I, and for M^{III}, Al, Fe^{III}, Cr^{III}, Mn^{III}, and Tl^{III}. We may even employ selenates, such as K_2SeO_4. All of the resulting double salts are isomorphous, and a crystal of one will continue to grow in a solution of another, acquiring, of course, an outer layer of different composition but of the same crystallographic orientation.

Potassium-Aluminium Sulphate. — Ordinary alum $K_2SO_4, Al_2(SO_4)_3, 24H_2O$ is made from aluminium sulphate obtained from clay (see above). It is also prepared by heating alunite, a basic alum found near Rome and in Hungary, and extracting the product with hot water. The alunite, having the composition $KAl_3(OH)_6(SO_4)_2$, leaves an insoluble residue of the hydroxide, mixed with ferric oxide which is present as an impurity:

$$2KAl_3(OH)_6(SO_4)_2 \rightarrow K_2SO_4, Al_2(SO_4)_3 + 4Al(OH)_3.$$

The aqueous solution of alum contains, at 10°, 9 parts of the anhydrous salt in 100 parts of water, and at 100° 422 parts in 100 of water. The hydrated salt melts at 90°. An aqueous solution of this salt or of sodium phosphate (p. 577) is used for fire-proofing draperies, because the crystals deposited in the fabric melt easily, and the fused material protects the fibers from access of oxygen. When heated more strongly alum loses its water of hydration together with some sulphur trioxide, and leaves a slightly basic, anhydrous salt known as "burnt alum." A solution of alum dissolves a considerable amount of aluminium hydroxide, giving "neutral alum," a basic salt $K_2SO_4, Al_4(OH)_6(SO_4)_3$ used as a mordant. The substance is usually prepared by adding sodium carbonate to the solution of alum as long as the aluminium hydroxide, formed locally, continues to redissolve.

Aluminium Sulphide. — This compound is most easily obtained by mixing pyrite with aluminium powder and igniting with magnesium ribbon (p. 684):

$$3FeS_2 + 4Al \rightarrow 2Al_2S_3 + 3Fe.$$

It forms a grayish-black solid, and is decomposed by water like magnesium sulphide, giving the hydroxide and hydrogen sulphide.

Aluminium Acetate. — This salt is used by dyers, because, being a salt of a weak base and a weak acid, it is much hydrolyzed by water, especially at 100°. In mordanting, it thus gives aluminium hydroxide very easily. It is made by treating lead or barium acetate with aluminium sulphate, and filtering and crystallizing the solution:

$$Al_2(SO_4)_3 + 3Ba(C_2H_3O_2)_2 \rightleftarrows 3BaSO_4\downarrow + 2Al(C_2H_3O_2)_3.$$

Dyeing: Mordanting. — The problem of the dyer is to confer the desired color upon a fabric made, usually, of cotton, linen, wool, or silk, and to do this in such a way that the dye is fast to (*i.e.*, is not removed or destroyed by) rubbing, and often, also, to washing with soap. To understand the means by which this is achieved, it must be noted that cotton and linen consist of hollow fibers of the composition of cellulose $(C_6H_{10}O_5)_x$. Wool is made of hollow fibers, also, and silk of rods, but the material is entirely different. It contains 17 per cent of nitrogen in the case of wool, and 20 per cent in the case of silk, and the nitrogen compounds of which the material is composed are much more active chemically than is cellulose, and combine incomparably more easily and firmly with the many kinds of organic compounds which are used as dyes. Hence, stains on wool and silk are much less often removable by washing than are those on cotton.

We have space to mention only three kinds of dyes and to describe in mere outline their use. These are:

1. **Insoluble colored bodies** which are formed by precipitation within the fibers and may be applied to any fabric, for their retention is due to mechanical and not to chemical causes. If cotton is boiled in a solution of lead acetate (or, better still, sodium plumbite, *q.v.*), and is then soaked in boiling potassium chromate solution, it is dyed a brilliant and permanent yellow. Lead chromate is the colored body:

$$Pb(C_2H_3O_2)_2 + K_2CrO_4 \rightleftarrows 2KC_2H_3O_2 + PbCrO_4\downarrow.$$

In indigo dyeing the fabric is saturated with a solution of indigo-white (an acid substance) in caustic soda, and is then exposed to the air. Indigo-blue is formed by oxidation, and, being insoluble, is precipitated in the fibers:

$$2C_{16}H_{12}N_2O_2 + O_2 \rightarrow 2C_{16}H_{10}N_2O_2\downarrow + 2H_2O.$$

2. We have **direct or substantive dyes**, which are withdrawn from a solution by the goods which are being dyed, and confer upon the latter a depth of color depending on the strength of the solution and the affinity of the material for the dye. The union is due in some cases to chemical combination, and in others to the fact that the dye is more soluble in the material being dyed than in water, and gives a solid solution in the former (*cf.* pp. 146, 235). When the case is simply one of extraction of the dye, due to the solvent power of the goods, the dye must necessarily be removed again by washing with sufficient water. Only a small minority of direct dyes are taken up by cotton or linen in such a way that they cannot be washed out. Congo red, $C_{32}H_{22}N_6S_2O_6Na_2$, is soluble in water, and is used in dyeing both cotton and wool. The dye is much faster on the latter than on the former, however.

3. The last class comprises the **mordant** or **adjective** dyes. They work on the principle that the cloth is first impregnated with a substance capable of attaching itself both to the cloth and, subsequently, to the dye also, and is then immersed in the dye itself. Substances of this kind are tannic acid (for basic dyes) and colloidal hydroxides (for acid dyes) like those of aluminium, tin, iron, and chromium. They are called **mordants** (Lat. *mordere*, to bite). When aluminium hydroxide is to be used, the cloth is first treated with a hot solution of neutral alum, aluminium sulphate, aluminium acetate, or sodium aluminate, and thereby acquires, either by adsorption or feeble combination, a certain amount of the hydroxide. The fabric is then boiled in water with the dye. If, for example, alizarine (madder) is used, the cloth is dyed Turkey red. Alizarine is an orange-yellow, very slightly soluble acid of the composition $C_{14}H_8O_4$. Since the color is that of the *compound* of the dye with the mordant, different mordants give different colors, or shades of color, with the *same* dye. This may be illustrated by preparing three solutions, one of ferric chloride (*q.v.*) containing ferric hydroxide in solution, one of aluminium acetate, and one of chromium acetate. When a drop or two of an alcoholic solution of alizarine is added to each, a precipitate at once appears, which in the first case is violet, in the second bright-red, and in the third claret-red. These insoluble compounds of dyes with mordants are identical with the coloring matters produced in the cloth, and are called **lakes** (Fr. *laque*, lac).

Kaolin and Clay: Earthenware and Porcelain. — By the action of water and carbon dioxide upon granite and other rocks con-

taining feldspar $KAlSi_3O_8$, the potash is slowly removed, and the compound changed largely into a hydrated orthosilicate $H_2Al_2(SiO_4)_2,H_2O$. When this remains *in situ*, it forms kaolin or china clay, a white, crumbly material. It usually contains particles of mica and free silica. When washed away and redeposited, it acquires compounds of iron, and more or less of the carbonates of calcium and magnesium, becoming common clay. Ocher, umber, and sienna are clays colored with oxides of iron and manganese. Fuller's earth is a purer variety.

On account of its plasticity when moist, and its tendency to become hard, but not to melt, when heated strongly, clay is used in making **bricks, pottery,** and **porcelain.** The presence of calcium and magnesium carbonates makes the clay more fusible, that of silica less so. Iron compounds cause it to turn red during firing. The impure varieties are formed into bricks and tiles, and are fired at a low temperature. The efflorescence which often appears on the surface of the bricks ("niter") is generally due to sodium sulphate or sodium chloride present originally in the clay. For earthenware, glazing must be applied to make the vessels water-tight. This is often done by throwing salt into the kiln. The hot steam hydrolyzes the salt to sodium hydroxide and hydrochloric acid, and the former combines with the clay, giving a fusible silicate which fills the pores of the surface. For porcelain, very pure clay, free from iron, is employed, and it is mixed with feldspar and quartz. The feldspar melts and fills the pores so that a continuous, semi-transparent material results. For china painting, powdered enamels (p. 607) and metallic oxides which combine with the clay, giving colored silicates, are used.

Porcelain, if made with sufficient silica, is very infusible. It is attacked by aqueous and by fused alkalies, however, giving soluble silicates.

Ultramarine was formerly obtained by pulverizing natural *lapis lazuli*. Artificial ultramarine of similar composition and more beautiful color is now manufactured. It is made by heating together kaolin, sodium carbonate, sulphur, and charcoal. The resulting green mass is then powdered, mixed with sulphur, and heated again until it acquires the desired shade. The product is used largely in making wall-papers, water-color paints, and laundry blue. Note-paper is often colored with it. Its composition is approximately $4NaAlSiO_4,Na_2S_2$, but the cause of the brilliant color is not understood. Hydrochloric acid liberates sulphur and hydrogen sulphide and destroys the color of ultramarine, decomposing, apparently, the sulphide of sodium.

Analytical Reactions of Aluminium Compounds. — The alkalies, and alkaline solutions like that of ammonium sulphide, precipitate the white hydroxide. The product is soluble in excess of the active alkalies. Soluble carbonates also throw down the hydroxide. Aluminium compounds, when heated strongly in the flame with cobalt salts, give a blue aluminate of cobalt.

Exercises. — 1. What are the differences between zinc and aluminium, and their corresponding compounds ?

2. Construct equations showing (*a*) the hydrolysis of aluminium sulphate (p. 686), (*b*) the interaction of aluminium sulphate and cobalt nitrate in the Bunsen flame.

3. Formulate the ionization of aluminium hydroxide (pp. 648, 684).

CHAPTER XL

GERMANIUM, TIN, LEAD

THE elements of the fifth column of the periodic table, aside from carbon and silicon, are germanium (Ge, at. wt. 72.5), tin (Sn, at. wt. 119), and lead (Pb, at. wt. 206.9). These are on the right side, while titanium (Ti, at. wt. 48.1), zirconium (Zr, at. wt. 90.6), cerium (Ce, at. wt. 140.25), and thorium (Th, at. wt. 232.5) occupy the left side.

The Chemical Relations of the Family. — All of these elements show a maximum valence of four. Germanium, tin, and lead are also bivalent. In this respect they resemble carbon and differ from silicon, which is more closely allied to the elements on the left side of the column. The oxides and hydroxides in which these three elements are bivalent become more basic, and the elements themselves more metallic in chemical relations, with increase in atomic weight. In this they resemble the potassium, calcium, and gallium families. Curiously enough, the same three hydroxides are also acidic. They are more strongly acidic than is zinc hydroxide, for the salts they form by interaction with bases are less hydrolyzed than are the zincates. This acidic character likewise increases in the order in which the elements are named above.

GERMANIUM.

Germanium (*cf.* p. 412) may be described as a transition element between carbon and tin. It forms two oxides GeO and GeO_2 corresponding to those of carbon and of tin. **Germanious oxide** is not very definitely basic or acidic, and the sulphide is the only other well-defined compound of this set. **Germanic oxide** and hydroxide are acidic entirely. The resemblance to carbon is shown in the formation of an unstable compound with hydrogen, and of **germanium chloroform** $GeHCl_3$. Like carbon, tin, and silicon, germanium gives a volatile **chloride** $GeCl_4$ (b.-p. 87°). Like tin and gold (p. 638), it forms **complex sulphides** derived from germanic sulphide, such as K_2GeS_3. The element was discovered (in 1886) in argyrodite, a complex sulphide $4Ag_2S, GeS_2$.

Tin.

The Chemical Relations of the Element. — Tin is both bivalent and quadrivalent. Each of the oxides and hydroxides SnO and $Sn(OH)_2$, SnO_2 and $SnO(OH)_2$ (or $Sn(OH)_4$), is both basic and acidic, so that there are really four series of compounds. Still, stannous hydroxide is mainly a base, of a feeble sort, while stannic hydroxide is mainly an acid. Thus we have stannous chloride, sulphate, and nitrate, which are stable, although they are all more or less hydrolyzed by water, and sodium stannite $Na_2.SnO_2$ which is unstable. On the other hand, stannic nitrate, sulphate, and chloride are completely hydrolyzed by water, while sodium stannate Na_2SnO_3 is comparatively stable. The dioxide SnO_2 is an infusible solid, and resembles, therefore, silicon dioxide. Tin has a tendency to give complex acids and salts, like H_2SnCl_6, $(NH_4)_2.SnCl_6$, H_2SnI_6, K_2SnF_6, but these are ionized also to a small extent after the manner of double salts, giving ions of $Sn^{\cdot\cdot\cdot\cdot}$. Tin forms no compounds with hydrogen and no salts with weak acids, like carbonic acid.

Occurrence and Extraction. — The chief ore of tin is tin-stone, or cassiterite SnO_2, which consists of tetragonal crystals whose dark color is due to the presence of iron compounds. The mineral occurs in Cornwall and the East Indies. The ore is roughly pulverized and washed, to remove granite or slate with which it is mixed, and is then roasted, to oxidize the sulphides of iron and copper, and drive off the arsenic which it contains. After renewed washing to eliminate sulphate of copper and oxide of iron, it is reduced with coal in a reverberatory furnace. The tin is afterwards remelted at a gentle heat, and the pure metal flows away from compounds of iron and arsenic. In 1900 the production was 4100 tons and 63,700 tons in England and in the East Indies, respectively. These quantities together constitute 83 per cent of the total world's output.

Physical and Chemical Properties. — Tin is a silver-white, crystalline metal of low tenacity but great malleability (tinfoil). Its specific gravity is 7.3, and its melting-point about 233°. Tin sometimes changes into a gray, pulverulent, specifically lighter modification (sp. gr. 5.85) when it is kept at a low temperature. The transition point is 20° (*cf.* Sulphur, p. 368), and ordinary tin, although it can be kept almost indefinitely, is therefore really in a metastable condition (p. 159) below this temperature.

Tin-plate (*cf.* p. 673) is made by dipping carefully cleaned sheets of mild steel into molten tin. Vessels of copper are also coated, internally, with tin, to prevent the formation of the basic carbonate (p. 618). For this purpose they are cleaned with ammonium chloride, sprinkled with rosin (to reduce the oxide), and heated to 230°. Molten tin is then spread on the surface with a piece of tow. Common pins are made of brass wire, and are coated with tin by being shaken in a solution containing a salt of this metal. The zinc in the alloy displaces some of the tin, and this is deposited on the surface of the brass. Alloys of tin, such as bronze (p. 619), soft solder (50 per cent lead), pewter (25 per cent lead), and britannia metal (10 per cent antimony and some copper), are much used in the arts.

Tin, although it displaces hydrogen from dilute acids, is not tarnished by moist air. *With warm hydrochloric acid it gives stannous* chloride $SnCl_2$ and hydrogen. Hot, concentrated sulphuric acid forms stannous sulphate $SnSO_4$ and sulphur dioxide. Nitric acid, when cold and dilute, interacts with it, giving stannous nitrate, and a portion of the nitric acid is reduced to ammonia (*cf.* p. 446):

$$4Sn + 10HNO_3 \rightarrow 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3.$$

With concentrated nitric acid, stannic nitrate is formed, but most of this salt is hydrolyzed by the water at the high temperature of the action (*cf.* p. 657), and metastannic acid $(H_2SnO_3)_5$ remains. The final result is therefore shown by the equation (simplified):

$$Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O.$$

The white, insoluble product continues to give nitric acid during prolonged washing, and seems therefore to contain some nitrate, or basic nitrate. Tin also displaces hydrogen from caustic alkalies, giving a metastannate, such as K_2SnO_3.

Stannous Chloride. — This salt is made by the interaction of tin and hydrochloric acid. *Evaporation of the solution gives the colorless* $SnCl_2,2H_2O$. When the crystals are heated, or when a strong aqueous solution is diluted, the salt is partially hydrolyzed. In the latter case the basic chloride Sn(OH)Cl is deposited. By presence of excess of hydrochloric acid, the hydrolysis is prevented. The solution is used as a mordant (p. 688).

Stannous chloride tends to pass into stannic chloride $SnCl_4$, and is therefore an active reducing agent. Thus, it reduces the chlorides of mercury (p. 655) and of the noble metals, liberating the free metals. The action is of the form $Hg^{\cdot\cdot} + Sn^{\cdot\cdot} \rightarrow Hg + Sn^{\cdot\cdot\cdot\cdot}$. Stannous chloride reduces cupric and ferric chlorides to the cuprous and ferrous conditions in like manner:

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4 \quad \text{or} \quad 2Fe^{\cdot\cdot\cdot} + Sn^{\cdot\cdot} \rightarrow 2Fe^{\cdot\cdot} + Sn^{\cdot\cdot\cdot\cdot}.$$

It also reduces free oxygen, or, what is the same thing, is oxidized by the air. In this case, stannic chloride is formed in the acid solution and the liquid remains clear; in the neutral solution a precipitate of the basic chloride is formed as well:

$$6SnCl_2 + 2H_2O + O_2 \rightarrow 4Sn(OH)Cl + 2SnCl_4.$$

Powdered tin, if placed in the bottle along with the acid solution, will undo the effects of this action by reducing the stannic salt to the stannous condition once more.

Stannic Chloride. — When chlorine acts upon tin, or upon stannous chloride (either solid or dissolved), stannic chloride is formed. The compound is a colorless liquid (b.-p. 114°) which fumes very strongly in moist air, giving hydrochloric acid and stannic acid. It was formerly known, after its discoverer (1605), as *spiritus fumans Libavii.* The aqueous solution, when freshly made, has almost no conductivity, and the compound is therefore very slightly ionized. As hydrolysis proceeds, the conductivity increases, but the hydrochloric acid is the conducting substance. After a time hydrolysis becomes almost complete. The stannic acid which is formed is not precipitated, however, but remains dissolved in colloidal (p. 523) form:

$$SnCl_4 + 4H_2O \rightleftarrows 4HCl + Sn(OH)_4.$$

The chloride, with small amounts of water, gives crystalline hydrates $SnCl_4,3H_2O$, $SnCl_4,5H_2O$, and $SnCl_4,8H_2O$, of which the second is used as a mordant under the name "oxymuriate" of tin. The double (or perhaps complex) salts $SnCl_4,2M^ICl$ are easily made. Ammonium-stannic chloride or "pink-salt" $(NH_4)_2SnCl_6$, which is an example of this class of compounds, is used as a mordant on cotton. It gives a red lake with alizarine (p. 689).

Stannic bromide $SnBr_4$ melts at 30°, boils at 201°, and is soluble in water.

α-Stannic Acid and its Salts. — When a solution of stannic chloride is treated with ammonium hydroxide, a white, gelatinous precipitate is formed. To this the formula H_2SnO_3 is generally assigned:

$$SnCl_4 + 4NH_4OH \rightarrow 4NH_4Cl + H_2SnO_3 + H_2O.$$

It is, however, in reality, a hydrogele, and loses water gradually until the dioxide remains. Thus, neither $Sn(OH)_4$ nor $SnO(OH)_2$ is obtainable as a definite compound. When stannic oxide is fused with caustic soda, the metastannate, or α-stannate, is formed:

$$SnO_2 + 2NaOH \rightarrow Na_2SnO_3 + H_2O.$$

This compound is obtainable as $Na_2SnO_3,3H_2O$, and is used as a mordant under the name of "preparing salt." When its solution is acidified, the above mentioned α-stannic acid is formed by double decomposition. This α-stannic acid interacts readily with acids and alkalies, and the chloride obtained from it is identical with stannic chloride described above.

The α-stannates of the metals, aside from those of potassium and sodium, like the silicates and carbonates which they much resemble, are all insoluble in water, and may be made by double decomposition.

β-Stannic Acid, or Metastannic Acid. — The product of the action of nitric acid upon tin is a hydrated stannic oxide like the foregoing substance, but is not identical with it. It is not easily soluble in alkalies. By boiling it with caustic soda, however, and then extracting with pure water, a soluble sodium β-stannate, $Na_2Sn_5O_{11}$, is obtained. β-stannic acid is also very slowly attacked by acids, and the chloride secured from it is not identical with the ordinary chloride. For these reasons it is supposed to be a hydrate of a polymer of stannic oxide $(SnO_2)_5$. When *fused* with caustic soda, it gives the same α-stannate as does the dioxide itself.

The difference between the properties of the two stannic acids was noticed by Berzelius (1811), and was the first case in which identity in composition was found not to be accompanied by identity in properties (*cf.* Isomers, p. 488).

The Oxides of Tin. — When stannous oxalate is heated in absence of air, **stannous oxide** remains: $SnC_2O_4 \rightarrow SnO + CO_2 + CO$. It is a black powder which burns in the air, giving the dioxide. The corresponding **hydroxide** $Sn_2O(OH)_2$ is formed by adding sodium carbonate

to stannous chloride solution. It is a white powder, easily dehydrated, and interacts with alkalies to give a soluble stannite, such as Na_2SnO_2. When the solution is boiled, tin is deposited, and sodium stannate is formed, the behavior resembling that of cuprous oxide when heated with acids (p. 622). With acids, the hydroxide gives stannous salts.

Stannic oxide is found in nature (p. 693), and may be made in pure form by igniting β-stannic acid. When heated, it becomes yellow, but recovers its whiteness when cooled (*cf.* Zinc oxide, p. 648). Prepared at a low temperature, it interacts easily with acids, but after strong ignition, is affected by them very slowly.

The Sulphides of Tin. — **Stannous sulphide** is obtained as a dark-brown precipitate when hydrogen sulphide is led into a solution of a stannous salt.

Stannic sulphide is formed likewise by precipitation, and is yellow in color. It is made also by heating together tin filings, mercury, sulphur, and ammonium chloride. The mercury and ammonium chloride are ultimately volatilized, and the stannic sulphide remains in the form of yellow, crystalline scales ("mosaic gold" or "bronze powder"). Stannic sulphide loses sulphur when strongly heated, and leaves stannous sulphide. It is not much affected by dilute acids, but interacts with solutions of ammonium sulphide or sodium sulphide, giving a soluble complex sulphide, the sulphostannate:

$$SnS_2 + (NH_4)_2S \rightarrow (NH_4)_2.SnS_3.$$

The corresponding sodium salt is easily crystallized in the form $Na_2SnS_3, 2H_2O$. Stannous sulphide is not affected by sulphides, but polysulphides, such as yellow ammonium sulphide, give with it the above mentioned sulphostannates:

$$SnS + (NH_4)_2S + S \rightarrow (NH_4)_2.SnS_3.$$

With acids the sulphostannates undergo double decomposition, but the free acid $H_2.SnS_3$ thus produced is unstable and breaks up, giving off hydrogen sulphide, and depositing stannic sulphide.*

Analytical Reactions of Salts of Tin. — The two ionic forms of tin, $Sn^{\cdot\cdot}$, and $Sn^{\cdot\cdot\cdot\cdot}$, are both colorless. Their behavior is different.

* These and similar compounds are often called thiostannates, orthothiantimonates, etc. The prefix sulpho- gives more euphonious words, however, and is used here for all excepting the thiocyanates.

They give a brown and a yellow sulphide, respectively, with hydrogen sulphide. The solubility of these sulphides in yellow ammonium sulphide distinguishes them (*cf.* p. 661) from those of cadmium, copper and other metals whose sulphides are similarly insoluble in dilute acids. The sulphides of arsenic, antimony, and gold (*q.v.*), however, behave like those of tin in this respect. The reducing power of distannion $Sn^{\cdot\cdot}$ is very characteristic (p. 695). Zinc displaces tin from solutions of its salts. The oxides are reduced by charcoal in the reducing part of the Bunsen flame and the metal is liberated.

LEAD.

The Chemical Relations of the Element. — Lead is both bivalent and quadrivalent. The oxides PbO and PbO_2, and the corresponding hydrated oxides, are both basic and acidic. Lead monoxide is a fairly active base, comparable with cupric oxide, and lead dioxide a feeble one. Both are feebly acidic. The salts of bivalent lead, like $Pb(NO_3)_2$, commonly called the plumbic salts, are somewhat hydrolyzed by water, but less so than are those of tin. The tetrachloride and other salts of quadrivalent lead are completely hydrolyzed. The plumbites $Na_2.PbO_2$ and plumbates $Na_2.PbO_3$ are hydrolyzed to a considerable extent. All the compounds in which lead is quadrivalent give up half of the negative radical readily, and are reduced to the "plumbic" condition. The metal displaces hydrogen with difficulty, and is easily displaced by zinc. Lead compounds are all poisonous, and the effects of repeated, very minute doses are cumulative — resulting in "lead colic."

Occurrence and Metallurgy. — Commercial lead is almost all obtained from galena PbS, which crystallizes in cubes. This ore often contains considerable amounts of silver sulphide Ag_2S, which is isomorphous with it, and it occurs in association with sulphides of arsenic, antimony, zinc, copper, and iron. Other salts of lead are of less common occurrence.

The sulphide of lead is first roasted until a sufficient proportion of it has been converted into the oxide and sulphate. The furnace-doors are then closed, and the temperature raised in order that these products may interact with the unchanged part of the sulphide:

$$PbS + 2PbO \rightarrow 3Pb + SO_2,$$
$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2$$

Ano ısists in heating galenite with scrap iron or iron ores and coal:

$$PbS + Fe \rightarrow Pb + FeS.$$

The molten ferrous sulphide rises to the top as a matte.

The purification of the lead from the other metals whose sulphides have been reduced at the same time is often troublesome. In Parke's process (p. 627) for the extraction of the silver by means of zinc, the greater part of the foreign metals, with the exception of bismuth, passes into the zinc scum. About 0.5 per cent of zinc remains in the lead, and is oxidized by the action of a jet of steam before the lead is poured into the molds. In one establishment, at Trail, near Rossland, B.C., the refining is carried out electrolytically. The lead is cast into plates, and the process is similar to that used for refining copper (p. 617). The bath is a solution of hydrofluosilicic acid containing hydrofluosilicate of lead. The less electro-positive metals, Cu, Sb, Bi, As, Ag, Au, with 10–16 per cent of lead, remain as a sort of skeleton of the anode, while Zn, Co, Ni, and Fe go into solution and are not redeposited.

Physical and Chemical Properties. — Metallic lead is gray in color, very soft, and of small tensile strength. Its specific gravity is 11.4, and its melting-point 326°. While warm, it is formed by hydraulic pressure into pipes which are used in plumbing and for covering electric cables. On account of its very slow interaction with most substances, sheet lead is used in chemical factories, for example, to line sulphuric-acid chambers. An alloy containing 0.5 per cent of arsenic is used in making small shot and shrapnel bullets. Type-metal contains 20–25 per cent of antimony (*q.v.*). In both cases greater hardness (*cf.* p. 532) is secured by the addition of the foreign metal.

Lead oxidizes very superficially in the air. The suboxide Pb_2O is supposed to be first formed. The final covering is a basic carbonate. Contact with hard waters confers upon lead a similar coating composed of the carbonate and the sulphate. These deposits, being insoluble, inclose the metal and protect the water from contamination with lead compounds. Pure rain-water, however, since it has no hardness, but contains oxygen in solution, gives the hydroxide $Pb(OH)_2$, which is noticeably soluble. When heated in the air, lead gives the monoxide PbO or minium Pb_3O_4, according to the temperature (see below).

The metal displaces hydrogen from hydrochloric acid very slowly. It is hardly affected by concentrated sulphuric acid, although, when the commercial acid is diluted with water, a slight precipitate of lead sulphate, acquired from the evaporating-pans, is thrown down. Nitric acid attacks it readily, giving lead nitrate and oxides of nitrogen (p. 446).

Chlorides and Iodide of Lead.—**Plumbic chloride** is precipitated when a soluble chloride is added to a solution of a soluble lead salt. It is slightly soluble in water (1.5 : 100) at 18°, and considerably more so at 100°. In the saturated solution at 25° about 50 per cent of the lead is in the form $Pb^{\cdot\cdot}$, 44 per cent as $PbCl^{\cdot}$, and 6 per cent as $PbCl_2$ (*cf.* p. 346).

Lead tetrachloride is a solid at −15°, and loses chlorine at the ordinary temperature. It is made by passing chlorine into plumbic chloride suspended in hydrochloric acid. The solution appears to contain H_2PbCl_6. With ammonium chloride this solution deposits crystals of a double or complex salt $PbCl_4,2NH_4Cl$ analogous to pink-salt (p. 695). When this is thrown into cold, concentrated sulphuric acid, an oil of the composition $PbCl_4$ settles to the bottom. The oil fumes in the air, and, in general, closely resembles stannic chloride $SnCl_4$. When dissolved in little water, it slowly deposits $PbCl_2$ and gives off chlorine. With much water it is quickly hydrolyzed, and lead dioxide is thrown down:

$$PbCl_4 + 2H_2O \rightarrow PbO_2 + 4HCl.$$

Lead iodide PbI_2 is yellow in color, and is formed by precipitation. It is somewhat soluble in boiling water, and crystallizes in yellow scales from the hot solution.

Plumbic chloride and iodide are both, under some conditions, more soluble in acids or salts with a common negative ion than they are in water, and form soluble, but somewhat unstable, complex salts (*cf.* p. 621).

Oxides and Hydroxides.—There are five different oxides of lead, Pb_2O, PbO, Pb_3O_4, Pb_2O_3, and PbO_2. The **suboxide** Pb_2O is a dark-gray powder, formed by gently heating the oxalate. **Plumbic oxide**, or lead monoxide PbO, is made by cupellation (p. 627) of lead, and the solidified, crystalline mass of yellowish-red color is sold as "litharge." The yellow, powdery form is called "massicot," and may

be obtained by heating the nitrate or carbonate. All the other oxides yield this one when they are heated above 600° in the air. Plumbic oxide takes up carbon dioxide from the air, and therefore usually contains a basic carbonate. It dissolves in warm sodium hydroxide solution, giving a plumbite $Na_2.PbO_2$; a saturated solution redeposits part of the oxide in crystalline form when it cools. The oxide is used in glass-making and for preparing salts of lead.

Plumbic hydroxide is formed by precipitation. It gives up water in three stages with different aqueous tensions (*cf.* p. 122), the products in the order of decreasing tension being $Pb(OH)_2$, $Pb_2O(OH)_2$, $Pb_3O_2(OH)_2$. These substances, as will be seen, are equivalent in composition to PbO, H_2O, $2PbO, H_2O$, and $3PbO, H_2O$ respectively. The hydroxide is observably soluble in water, and gives a solution with a faintly alkaline reaction. With acids it forms salts of lead. It interacts also with potassium and sodium hydroxides to form the soluble **plumbites**, like $Na_2.PbO_2$.

Minium, or **red lead**, Pb_3O_4, gives off oxygen when heated:

$$2Pb_3O_4 \rightleftarrows 6PbO + O_2.$$

The dissociation pressure varies with the temperature:

Temperature	445°	500°	555°	636°
Pressure in mm.	5	60	183	763

Since the partial pressure of oxygen in the air is 150 mm., the substance decomposes at about 550°. It can be formed in air by reversal of the action represented above, but only below this temperature (*cf.* p. 591). In pure oxygen of one atmosphere pressure it could be formed at 600°, but not at 650°. On account of unequal heating during manufacture, commercial red lead is never fully oxidized, and always contains litharge. Conversely, commercial litharge usually contains a little minium.

Minium, when heated with warm, dilute nitric acid, is decomposed, and leaves lead dioxide as an insoluble powder. It is therefore regarded as lead orthoplumbate (see below):

$$Pb_2.PbO_4 + 4HNO_3 \rightleftarrows 2Pb(NO_3)_2 + H_4PbO_4.$$

The double decomposition as a salt that it thus undergoes is followed by dehydration of the plumbic acid, which is unstable ($H_4PbO_4 \rightarrow PbO_2 + 2H_2O$), and the dioxide remains. Red lead is used in glass-

making, and, when mixed with oil, gives a red paint which is specially applicable to iron-work (*cf.* p. 658).

Lead dioxide may be obtained as described above in the form of a brown powder. Unlike most oxides, it is a conductor of electricity. It is usually made by adding bleaching powder to an alkaline solution of plumbic hydroxide:

$$Na_2.PbO_2 + Ca(OCl)Cl + H_2O \rightarrow 2NaOH + CaCl_2 + PbO_2\downarrow.$$

In this action we may regard the free lead hydroxide, formed by hydrolysis of the plumbite, as being oxidized by the bleaching powder. This dioxide is an active oxidizing agent. It interacts with, and sets fire to, a stream of hydrogen sulphide, and it liberates chlorine from hydrochloric acid. With acids it gives no hydrogen peroxide, and is not a peroxide in the restricted sense of the term (p. 308). Lead dioxide interacts with potassium and sodium hydroxides, giving soluble **plumbates**. These are derived from metaplumbic acid. The potassium salt $K_2PbO_3,3H_2O$ is analogous to the metastannate $K_2SnO_3,3H_2O$ (p. 696). A mixture of calcium carbonate and lead monoxide absorbs oxygen when heated in a stream of air, and the yellowish-red calcium orthoplumbate is formed:

$$4CaCO_3 + 2PbO + O_2 \rightleftarrows 2Ca_2PbO_4 + 4CO_2.$$

The action is reversible, and is at the basis of Kassner's method of manufacturing oxygen from the air.

The Storage Battery. — In the storage battery the plates consist of leaden gratings, the openings of which are filled with the active materials, and the fluid is dilute sulphuric acid. When the battery discharges, the SO_4'' ions migrate towards those plates (usually the outer ones) which are filled with finely divided lead, and convert this into a mass of (insoluble) lead sulphate: $SO_4'' + Pb \rightarrow PbSO_4 + 2\ominus$. These plates receive therefore negative charges. Simultaneously the $H^{\cdot}$ ions pass towards the other plates, and reduce to monoxide the lead dioxide with which they are filled:

$$2H^{\cdot} + PbO_2 \rightarrow H_2O + PbO + 2\oplus.$$

These plates acquire positive charges, and, by secondary interaction of the monoxide with the sulphuric acid, become filled, like the negative

plates, with lead sulphate. During the discharge the fluid thus loses much sulphuric acid, and acquires a lower specific gravity, a fact by means of which the approach of complete discharge may be ascertained. The E.M.F. of the current is about 2 volts.

When a current, opposite in direction to the one which it yields, is led into the exhausted cell, the negative terminal of the dynamo circuit being connected with the negative pole of the battery and the positive with the positive, a new set of changes occurs. The $H^{\cdot}$ ions of the bath are attracted to the plate which has the negative charge, and an equivalent number of SO_4'' ions are formed, so that only metallic lead remains:

$$PbSO_4 + 2H^{\cdot} + 2 \ominus \rightarrow Pb + 2H^{\cdot} + SO_4''.$$

To express this otherwise, the hydrogen here reduces the lead sulphate (which is white) to metallic lead (a black powder). Simultaneously the SO_4'' is attracted to the positively charged plate, and forms lead persulphate with the lead sulphate there present: $SO_4'' + PbSO_4 + 2 \oplus \rightarrow Pb(SO_4)_2$. The lead persulphate, however, in a battery which is working normally, is at once hydrolyzed, and the filling of the plate is changed into lead dioxide: $Pb(SO_4)_2 + 2H_2O \rightarrow PbO_2 + 2H_2SO_4$. Both plates are thus brought back to the condition in which they were before the discharge.

The set of changes last described, that involved in the operation of charging, consumes energy, while the changes connected with the discharging, liberate energy. The whole may be put into a single equation:

$$2PbSO_4 + 2H_2O \underset{\leftarrow \text{ Discharge}}{\overset{\text{Charge} \rightarrow}{\rightleftarrows}} Pb + 2H_2SO_4 + PbO_2.$$

Lead Nitrate. — This salt may be made by treating lead, lead monoxide, or lead carbonate with nitric acid. It forms white, anhydrous octahedra. The nitrate and acetate (see below) are the salts of lead which, because of their solubility, are most commonly used. The solubility of the nitrate is, 48 parts in 100 at 10°, and 153 parts in 100 at 100°. Since the solubility increases with rise in temperature, we should expect the process of solution to be accompanied by absorption of heat (p. 260), and this is found to be the case. On account of hydrolysis, the solution is acid in reaction.

Lead Carbonate. — This compound is found in nature in rhombic crystals isomorphous with those of aragonite. It may be formed as a precipitate by adding a soluble bicarbonate to lead nitrate solution. With normal sodium carbonate, a basic carbonate $Pb_3(OH)_2(CO_3)_2$ is deposited. This basic salt is identical with **white lead**, which, on account of its superior opacity, has better covering power than zinc-white (p. 648) or permanent white (p. 610). The substance is manufactured in various ways, all of which involve the oxidation of the lead by the air, the formation of a basic acetate by the interaction of vinegar or acetic acid with the oxide, and the subsequent decomposition of the salt by carbon dioxide. The best quality is obtained by the Dutch method. In this, gratings of cast lead are placed above a shallow layer of vinegar in small pots. These pots are buried in manure, which by its decomposition furnishes the carbon dioxide and the necessary warmth. The gratings are gradually converted into a white mass of the basic carbonate. The vapor of acetic acid arising from the vinegar may be regarded as a catalytic agent (*cf.* p. 508), since it is used over and over again.

Lead Acetate. — This salt is made by the action of acetic acid on litharge, and crystallizes in prisms of the composition $Pb(C_2H_3O_2)_2$, $3H_2O$. It is easily soluble in water, and, from the sweet taste of the solution, is named **sugar of lead** (used in medicine). The basic salt $Pb(OH)(C_2H_3O_2)$ is formed by boiling a solution of lead acetate with excess of litharge. Unlike most basic salts, this basic salt is soluble in water, and its solution has a faintly alkaline reaction.

Lead Sulphate. — The sulphate occurs in nature as anglesite, and is isomorphous with heavy spar. Being insoluble in water, it is easily obtained by precipitation. It is slightly soluble in concentrated sulphuric acid (p. 387). It is dissolved to a noticeable extent by nitric acid, since this acid is more active than sulphuric acid (*cf.* p. 601). It is also soluble in concentrated sodium hydroxide solution, on account of the removal of the $Pb^{\cdot\cdot}$ ions which are a factor in its solubility product and their passage into the PbO_2'' anion of sodium plumbite (*cf.* p. 621). Finally, it dissolves easily in ammonium tartrate, since lead enters into the complex anion of the tartrates in the same way that copper does (*cf.* p. 623). Barium sulphate, which is of the same order of insolubility as lead sulphate, is somewhat affected by nitric acid, but not by sodium hydroxide or by tartrates. The element barium lacks both the characteristics which lead here exhibits.

Lead Sulphide. — Natural lead sulphide (galena) is black, and its crystals have a silvery luster. The precipitated salt is black and amorphous. It is more easily attacked by active acids than is mercuric sulphide (*cf.* p. 651). Concentrated nitric acid, being an oxidizing agent as well as an acid, attacks and dissolves it readily.

Analytical Reactions of Lead Compounds. — Hydrogen sulphide precipitates the black sulphide, even when dilute acids are present. Sulphuric acid throws down the sulphate. Potassium hydroxide gives the white hydroxide, which dissolves in excess to form the plumbite. Potassium chromate or dichromate (*q.v.*) gives a yellow precipitate of lead chromate $PbCrO_4$, which is used as a pigment under the name of "chrome-yellow."

Titanium, Zirconium, Cerium, Thorium.

The metals on the left side of the fifth column of the periodic table are all quadrivalent, although compounds in which a lower valence appears are numerous in this family. The first two are feebly base-forming as well as feebly acid-forming; the last two are base-forming exclusively.

Titanium occurs in rutile $TiTiO_4$. Derived from it are a number of titanates of the form K_2TiO_3, titanic iron ore (menaccanite) being ferrous titanate $FeTiO_3$.

Zirconium is found in zircon, the orthosilicate of zirconium $ZrSiO_4$, which occurs in square prismatic crystals isomorphous with rutile, cassiterite ($SnSnO_4$), pyrolusite ($MnMnO_4$), and thorite ($ThSiO_4$). The oxide is used in making the incandescent substance in some forms of gas lamps.

Cerium occurs chiefly in cerite [Ce, La, Nd, Pd]SiO_4, H_2O.

Thorium is found in thorite $ThSiO_4$ but most of the supply comes from monazite sand. The nitrate $Th(NO_3)_4, 6H_2O$ is used in making Welsbach incandescent mantles (*cf.* Flame, p. 510). The mantle of knitted cotton is dipped in a solution of this salt along with one per cent of cerium nitrate $Ce(NO_3)_4$, and is then ignited. The oxides ThO_2 (thoria) and CeO_2 (ceria) which remain form a fairly coherent mass. Larger or smaller proportions of cerium oxide diminish the luminosity of the glowing material. It is supposed that the particles of finely divided cerium oxide assist the union of the oxygen and illuminating-gas catalytically and hence are themselves raised to a high temperature by the

action which is thus concentrated in their neighborhood. The thoria acts simply as a nonconducting support for the ceria.

The **Nernst lamp** is an incandescent electric lighting arrangement in which a rod of the oxides of several of the rare metals takes the place of the common carbon filament. The peculiarity of this lamp is that preheating is required before the rod attains a temperature at which it will conduct the current. When this point has been once reached, the resistance enables the current to maintain the rod at the temperature of incandescence. For equal consumptions of electricity, this form of electric lamp gives a greater yield of light than does the ordinary, carbon-filament, incandescent bulb.

Exercises. — 1. In what order should you place the elements dealt with in this chapter, beginning with the least metallic, and ending with the most metallic (p. 533)?

2. Construct equations showing (*a*) the interaction of tin and concentrated sulphuric acid, (*b*) of water and stannous chloride, (*c*) of chlorauric acid and stannous chloride (p. 695), (*d*) of oxygen and stannous chloride in acid solution, (*e*) the decomposition of lead oxalate (p. 700), (*f*) the interaction of lead monoxide and acetic acid, (*g*) and of lead monoxide and lead acetate.

3. To which class of ionic actions do the reductions by stannous chloride belong?

4. What interactions probably occur when lead dioxide liberates chlorine from hydrochloric acid?

5. How should you set about preparing (*a*) lead oxalate (insoluble), (*b*) lead chlorate (soluble)?

6. Should the formula of the sulphate of quadrivalent lead be written $Pb(SO_4)_2$ or PbS_2O_8, and is it related to persulphuric acid ($H_2S_2O_8$)?

7. Describe in terms of the categories used in connection with the phase rule (p. 592) the system furnished by minium at 500°.

CHAPTER XLI

ARSENIC, ANTIMONY, BISMUTH

THIS family is very closely related to the elements phosphorus and nitrogen which precede it in the same column of the periodic table. In reading this chapter, therefore, constant reference should be made to the chemistry of the corresponding compounds of phosphorus. A general comparison of the elements arsenic (As, at. wt. 75), antimony (Sb, at. wt. 120.2) and bismuth (Bi, at. wt. 208.5) with each other and with the two already disposed of will be given at the end of this chapter. It is sufficient here to say that arsenic is mainly an acid-forming element, and is therefore a non-metal, while antimony is both acid-forming and base-forming, and bismuth is base-forming. Each of the three elements gives sets of compounds in which it is trivalent, and others in which it is quinquivalent. None of the free elements displaces hydrogen from dilute acids.

ARSENIC.

The Chemical Relations of the Element. — Arsenic forms a compound with hydrogen AsH_3. It gives several halogen derivatives of the type AsX_3 which are completely hydrolyzed by water. Its oxides and hydroxides are acidic. Salts derived from H_3AsO_3 ($= As_2O_3, 3H_2O$) and $HAsO_2$ ($= As_2O_3, H_2O$), and named orthoarsenites and metarsenites, are known, as are also salts derived from various arsenic acids:

$$\begin{aligned} H_3AsO_4 &= As_2O_5, 3H_2O = AsO(OH)_3, \\ H_4As_2O_7 &= As_2O_5, 2H_2O = As_2O_3(OH)_4, \\ HAsO_3 &= As_2O_5, H_2O = AsO_2(OH). \end{aligned}$$

In analogy to the phosphates (p. 465), these are named ortho-, pyro- and metarsenates respectively. The last column shows a method of writing the formulæ which is often adopted (*cf.* p. 470). Sulphates, nitrates, carbonates, and other salts of arsenic are not formed. There are, however, complex sulphides of the forms $Na_3.AsS_3$ (sodium orthosulpharsenite), $Na_3.AsS_4$ (sodium orthosulpharsenate), etc.

In many natural sulphides, such as pyrite FeS_2 and zinc-blende

ZnS, a part of the sulphur is replaced by arsenic, which must therefore be playing the part of a bivalent element in such cases. When much arsenic is present, the formulæ are written thus: $Fe[S,As]_2$ and $Zn[S,As]$.

Occurrence and Preparation. — Arsenic is found free in nature. It occurs also in combination with many metals, particularly in arsenical pyrites FeAsS. Two sulphides of arsenic, orpiment As_2S_3 and realgar As_2S_2, and an oxide, white arsenic As_2O_3, are less common.

The element is obtained either from the native material or by heating arsenical pyrites: $FeAsS \rightarrow FeS + As$. During the roasting of the sulphur ores of metals, arsenic trioxide is formed by the oxidation of the arsenic so frequently present, and collects as a dust in the flues.

Physical Properties. — In its ordinary condition, the free element is steel-gray in color, metallic in appearance, and crystalline in form. When the vapor is suddenly cooled, however, a yellow variety is obtained, which is soluble in carbon disulphide, is phosphorescent in the air, and in other ways resembles common phosphorus. This, like yellow phosphorus, is the less stable form.

Elementary arsenic is easily volatilized at 180°, and acquires a vapor pressure of 760 mm. long before the melting-point (480°, under high pressure) is reached. The density of the vapor measured at 644° gives 308.4 as the weight of the G.M.V. (22.4 liters at 0° and 760 mm.). The weight combining with one chemical unit weight (35.45 g.) of chlorine, is 75 g., and this is the amount of the element found in the G.M.V. of the vapor of the chloride. It is also the smallest weight found in the G.M.V. of any volatile compound of arsenic, and is therefore accepted as the atomic weight. Since 308.4 is equal approximately to 4×75 (= 300), the formula of the vapor of the simple substance at 644° is As_4. At 1700° dissociation has occurred, and the formula is As_2 (*cf.* p. 206).

Chemical Properties. — The free element burns in the air, producing clouds of the solid trioxide As_2O_3. It unites directly with the halogens, with sulphur, and with many of the metals. When boiled with nitric acid, chlorine water, and other powerful oxidizing agents, it is oxidized in the same way as is phosphorus, and yields arsenic acid H_3AsO_4.

Arsine. — This substance corresponds in composition to ammonia and phosphine, and some of the ways in which it may be formed are analogous to those used in the case of these substances. Thus, when arsenic and zinc are melted together in the proportions to form zinc arsenide Zn_3As_2, and the product is treated with dilute hydrochloric acid, the result is similar to the action of water or dilute acids upon calcium phosphide. Arsine in fairly pure condition is evolved as a gas:

$$Zn_3As_2 + 6HCl \rightarrow 2AsH_3 + 3ZnCl_2.$$

Arsine is formed also by the action of nascent hydrogen (*cf.* p. 423) upon soluble compounds of arsenic, such as arsenious chloride $AsCl_3$ or arsenic acid. When a solution of one of these substances is added to zinc and hydrochloric acid in a generating flask, the disagreeable odor of the hydrogen evolved shows the presence of the arsine:

$$AsCl_3 + 6H \rightarrow AsH_3 + 3HCl.$$

This method, naturally, does not furnish pure arsine, for free hydrogen predominates in the gas. Pure arsine may be secured by leading the mixture with hydrogen through a U-tube immersed in liquid air. The arsine (b.-p. $-40°$) condenses as a colorless liquid.

Arsine burns with a bluish flame, producing water and clouds of arsenic trioxide: $2AsH_3 + 3O_2 \rightarrow 3H_2O + As_2O_3$. The combustion of hydrogen containing arsine produces the same substances. Since arsine, when heated, is readily dissociated into its constituents (*cf.* p. 252), the vapor of free arsenic is present in the interior of the hydrogen flame. This arsenic may be condensed in the form of a metallic-looking, brownish stain by interposition of a cold vessel of white porcelain. Even when only a trace of the compound of arsenic has been added to the materials in the generator, the stain which is produced is very conspicuous. This behavior thus furnishes us with an exceedingly delicate test — **Marsh's test** — for the presence of arsenic in any soluble form of combination. The compounds of antimony alone show a similar phenomenon (see Stibine). In carrying out the test, a tube of hard glass is attached to the generator, and is heated, by means of a Bunsen flame, at a point near to the flask. With this arrangement the arsenic is deposited in the form of a dark, lustrous ring just beyond the heated part. Zinc of special purity must be employed for generating the hydrogen, as all common specimens of the metal contain a sufficient amount of arsenic to give the metallic

film without any special addition of an arsenic compound, and a blank experiment must be run, with other portions of the same reagents, to guard against the possibility of its coming from any of them.

Arsine is exceedingly poisonous, the breathing of small amounts producing fatal effects. It differs from ammonia more markedly than does phosphine, for it is not only without action on acids, but does not unite directly even with the halides of hydrogen.

Halides of Arsenic. — The representatives of this class include a liquid trifluoride AsF_3, a pentafluoride, which is obtained only as a double compound with potassium fluoride, a liquid trichloride $AsCl_3$, a solid tribromide $AsBr_3$, and a solid tri-iodide AsI_3.

The **trichloride**, which is prepared by passing chlorine gas into a vessel containing arsenic, is easily formed as the result of a vigorous action. It is a colorless liquid, boiling at 130°. When mixed with water it is at once converted into the white, almost insoluble trioxide. The action is presumably similar to that of water upon the corresponding compound of phosphorus (p. 181), but the arsenious acid for the most part loses water and forms the insoluble anhydride:

$$AsCl_3 + 3H_2O \rightleftarrows As(OH)_3 + 3HCl,$$
$$2As(OH)_3 \rightleftarrows As_2O_3\downarrow + 3H_2O.$$

This action, however, differs markedly from the other in that it is reversible, and arsenic trioxide interacts with aqueous hydrochloric acid, giving a solution of arsenious chloride. When this solution is boiled, the volatility of the arsenious chloride causes it to be carried over with the hydrochloric acid (b.-p. 110°, *cf.* p. 182), and this method of separating arsenic from other substances is used in chemical analysis.

Oxides of Arsenic. — Two oxides are known — the trioxide As_2O_3 and the pentoxide As_2O_5. **Arsenic trioxide** is produced by burning arsenic in the air and during the roasting of arsenical ores (p. 708), and is known as "white arsenic" or simply "arsenic." It is purified for commercial purposes by subliming the flue-dust in cylindrical pots. The pure trioxide is deposited in the glassy form in the upper part of the vessel. It passes slowly from this amorphous condition into the common crystalline variety. Its vapor density indicates that it possesses the molecular weight As_4O_6, but the simpler formula expresses its chemical properties sufficiently well.

When treated with water, the trioxide dissolves to a very slight extent (0.3 : 100), forming arsenious acid, by reversal of the second of the equations given above. As usual, the less stable, amorphous variety is the more soluble (1 : 100). In boiling water the solubility is eventually much greater (11.5 : 100), but a condition of equilibrium is reached very slowly. With concentrated sulphuric acid the trioxide forms a sulphate of rather complex composition, indicating that it has basic properties, but this sulphate is decomposed into the oxide and sulphuric acid when treated with water. When heated in a tube with carbon, this oxide is reduced, and the free element, being volatile, is deposited upon the cold part of the tube just above the flame. It is an active poison, since it gradually passes into solution, forming arsenious acid.

The **pentoxide** is a white crystalline substance, formed by heating arsenic acid:

$$2H_3AsO_4 \rightarrow As_2O_5 + 3H_2O.$$

When raised to a higher temperature, it loses a part of its oxygen, leaving the trioxide. In consequence of this instability, it cannot be formed by direct union of oxygen with the trioxide, after the manner of phosphorus pentoxide.

Acids of Arsenic. — When elementary arsenic or arsenious oxide is treated with concentrated nitric acid, or with chlorine and water, **arsenic acid** is produced. The substance, which is a deliquescent white solid, possesses a composition similar to that of orthophosphoric acid, and when heated loses water in progressive stages, furnishing intermediate acids — pyroarsenic acid and metarsenic acid — and finally the pentoxide. The relationship of the substances (*cf.* p. 465) is shown by the formulæ: $H_3AsO_4 \rightarrow H_4As_2O_7 \rightarrow HAsO_3 \rightarrow As_2O_5$. These acids, however, differ from the corresponding compounds of phosphorus in that upon solution in water they *immediately* pass back into the ortho-acid. The final elimination of all the water by simple heating is also impossible with metaphosphoric acid. Many salts of these acids are known, those of orthoarsenic acid being isomorphous with the corresponding salts of phosphoric acid. The reddish-brown silver orthoarsenate and the white $MgNH_4AsO_4$ resemble the corresponding phosphates in being insoluble in water.

Arsenious acid, like sulphurous and carbonic acids, loses water, and yields the anhydride, arsenic trioxide, when the attempt is made to obtain it from the aqueous solution. The potassium and sodium

arsenites, K_3AsO_3 and Na_3AsO_3, are made by treating arsenic trioxide with caustic alkalies, and are much hydrolyzed by water. The arsenites of the heavy metals are insoluble, and can be made by precipitation. Paris green and Scheele's green (p. 624) are arsenites of copper. The poisonous effects of wall-paper colored with these compounds seem to be due to volatile organic derivatives of arsine which are formed by the action of a mold. In cases of poisoning by white arsenic, freshly precipitated ferric hydroxide or magnesium hydroxide is administered, since by interaction with the arsenious acid they form insoluble arsenites. The salts of arsenious acid are readily oxidized, passing into arsenates. The action of a standard solution of iodine upon sodium arsenite, for example, is used in volumetric analysis:

$$Na_3AsO_3 + H_2O + I_2 \rightleftarrows Na_3AsO_4 + 2HI.$$

Sulphides of Arsenic. — Three sulphides of arsenic are known, As_2S_5, As_2S_3, As_2S_2. The first, **arsenic pentasulphide**, is obtained as a yellow powder by decomposition of the sulpharsenates (see below), and by leading hydrogen sulphide into a solution of arsenic acid in concentrated hydrochloric acid. The latter action seems to show that the ion $As^{\cdot\cdot\cdot\cdot\cdot}$, derived from $AsCl_5$, is present in the solution.

Arsenious sulphide As_2S_3 occurs in nature as orpiment, and was formerly used as a yellow pigment (*auripigmentum*). The word arsenic is derived from the Greek name for this mineral (ἀρσενικόν). It is obtained as a citron-yellow precipitate when hydrogen sulphide is led into an aqueous solution of arsenious chloride. The slowness with which the precipitate appears is due to the temporary formation of a colloidal solution of the sulphide. When arsenious acid solution is employed, the precipitation may be delayed for days. A beam of light falling upon the solution is dispersed, and the liquid is thus shown to be filled with minute particles, which ultimately collect in flocculent form.

Realgar As_2S_2 is a natural sulphide of orange-red color, and is also manufactured by subliming a mixture of arsenical pyrites and pyrite:

$$2FeAsS + 2FeS_2 \rightarrow 4FeS + As_2S_2\uparrow.$$

It burns in oxygen, forming arsenious oxide and sulphur dioxide, and is mixed with potassium nitrate and sulphur to make "Bengal lights."

Sulpharsenites and Sulpharsenates. — The sulphides of arsenic interact with solutions of alkali sulphides after the manner of

the sulphides of tin (p. 697), giving soluble, complex sulphides. Arsenious sulphide with colorless ammonium sulphide gives ammonium sulpharsenite, and with the yellow sulphide gives ammonium sulpharsenate:

$$3(NH_4)_2S + As_2S_3 \rightarrow 2(NH_4)_3AsS_3,$$
$$3(NH_4)_2S + As_2S_3 + 2S \rightarrow 2(NH_4)_3AsS_4.$$

Proustite (p. 626) is a natural sulpharsenite of silver.

There are also metasulpharsenites and pyro- and metasulpharsenates of the forms $KAsS_2$, $K_4As_2S_7$, and $KAsS_3$. In fact, there are sulpho-compounds corresponding to all the forms of the oxygen acids. The particular products present in any solution depend on the concentrations used in making it. The formation of these soluble compounds is used in analysis (*cf.* p. 661).

Since these salts in solution furnish the ions AsS_3''' and AsS_4''', which with hydrogen ions give a feebly ionized sulpho-acid, they are decomposed by acids, and give free sulpharsenious or sulpharsenic acid:

$$(NH_4)_3AsS_3 + 3HCl \rightarrow H_3AsS_3 + 3NH_4Cl,$$
$$(NH_4)_3AsS_4 + 3HCl \rightarrow H_3AsS_4 + 3NH_4Cl.$$

These sulpho-acids, however, are unstable, and at once break up, giving hydrogen sulphide as a gas, and the sulphides of arsenic as yellow precipitates:

$$2H_3AsS_3 \rightarrow 3H_2S + As_2S_3,$$
$$2H_3AsS_4 \rightarrow 3H_2S + As_2S_5.$$

Antimony.

The Chemical Relations of the Element. — Antimony resembles arsenic in forming a hydride SbH_3 and halides of the forms SbX_3 and SbX_5. The latter are partially hydrolyzed by water with ease, but complete hydrolysis is difficult to accomplish with cold water. The oxide Sb_2O_3 is basic as well as feebly acidic, and the oxide Sb_2O_5 is acidic. Aside from the salts derived from the oxide Sb_2O_3, such as $Sb_2(SO_4)_3$, the compositions of the compounds are similar to those of the compounds of arsenic. The element gives complex sulphides like those of arsenic.

Occurrence and Preparation. — Antimony is found free in nature to a small extent. The chief supply, however, is furnished

by the black trisulphide Sb_2S_3, known as stibnite, which is found in Hungary and Japan, and forms shining, prismatic crystals of the rhombic system.

Native stibnite is roasted in the air in order to remove the sulphur, and the white oxide which remains is mixed with carbon and reduced by strong heat:

$$Sb_2S_3 + 5O_2 \rightarrow Sb_2O_4 + 3SO_2,$$
$$Sb_2O_4 + 4C \rightarrow 2Sb + 4CO.$$

Properties. — Antimony is a white, crystalline metal. It is brittle, and easily powdered. Its vapor at 1640° has a density corresponding to the formula Sb_2, while at lower temperatures Sb_4 is present. It is used in making alloys such as type-metal, stereotype-metal, and britannia metal (*q.v.*). The alloys of antimony expand during solidification, and therefore give exceptionally sharp castings.

The element unites directly with the halogens. It does not rust, but when heated it burns in the air, forming the trioxide Sb_2O_3 or a higher oxide Sb_2O_4. When heated with nitric acid, it yields the trioxide or antimonic acid (H_3SbO_4), according to the concentration of the nitric acid and the temperature employed. When heated with concentrated sulphuric acid, it forms the sulphate $Sb_2(SO_4)_3$.

Stibine. — The antimonide of hydrogen SbH_3 is formed by the action of zinc and hydrochloric acid on a soluble compound of antimony. By the action of dilute, cold hydrochloric acid on an alloy of antimony and magnesium (1 : 1), a mixture of hydrogen and stibine containing as much as 11.5 per cent (by volume) of the latter may be made. It is separated by cooling with liquid air, and gives a liquid boiling at $-18°$ and freezing at $-91.5°$. It is more easily dissociated than arsine, and forms a deposit of antimony when a porcelain vessel is held in the flame or when the gas passes through a heated tube. The behavior under this treatment is in all respects similar to that of arsine (p. 709).

The layers of arsenic or antimony obtained upon white porcelain in Marsh's test (p. 709) may be distinguished readily in several ways. The arsenic spots are brownish in color, lustrous, and volatile. The antimony spots are black, smoky-looking, and involatile at the temperature of the Bunsen flame. The arsenic spots dissolve in dilute nitric acid, while those of antimony do not. The arsenic spots dissolve in a fresh solution of bleaching powder, producing calcium chloride and

arsenic acid, while those of antimony are unaffected. The arsenic spots are scarcely attacked by a solution of yellow ammonium sulphide, while those of antimony dissolve readily, forming an ammonium sulphantimoniate. Another distinction between arsine and stibine is found in their action upon a solution of nitrate of silver. Stibine precipitates a silver antimonide Ag_3Sb, and none of the antimony remains in the solution. Arsine, on the contrary, precipitates metallic silver, while arsenious acid remains in the solution.

Antimony Halides. — The halogen compounds of antimony which are known include the trichloride, a solid melting at 73°; the pentachloride, a liquid; the tribromide, tri-iodide, trifluoride, and pentafluoride.

Antimony trichloride $SbCl_3$ is the most familiar of these substances. It forms large, soft crystals, and used to be named "butter of antimony." When treated with water, it forms a white, opaque, insoluble basic salt. When little water is used, the product is antimony oxychloride:

$$SbCl_3 + H_2O \rightleftarrows SbOCl\downarrow + 2HCl.$$

With a large amount of water, a greater proportion of the chlorine is removed, and $Sb_4O_5Cl_2$ ($= 2SbOCl,Sb_2O_3$) remains. With boiling water the oxide is finally formed. The action is not complete as long as hydrochloric acid is present. It may therefore be reversed, so that on addition of hydrochloric acid to the mixture, a clear solution of the trichloride is re-formed. If the concentration of the acid is once more reduced by dilution with water, the oxychloride is again precipitated.

The **pentachloride** is formed by leading chlorine over the trichloride. It is a liquid (b.-p. 140°) which fumes strongly in the air, being hydrolyzed by the moisture.

Oxides of Antimony. — Three oxides are known: antimony trioxide Sb_2O_3, antimony pentoxide Sb_2O_5, and an intermediate oxide Sb_2O_4. The **trioxide** is obtained by oxidizing antimony with nitric acid, or by combustion of antimony with a limited supply of oxygen. It is a white substance, insoluble in water. It is in the main a basic oxide, interacting with many acids to form salts of antimony. The **pentoxide** is a yellow, amorphous substance, obtained by heating antimonic acid. It combines with bases to form salts, and is therefore an acid-forming oxide exclusively. The intermediate compound Sb_2O_4 is

formed by heating antimony or the trioxide in oxygen. It is the most stable of the three oxides. It is neither acid- nor base-forming, and may be antimoniate of antimony ($SbSbO_4$).

The hydrated trioxide $Sb(OH)_3$ may be obtained as a white precipitate by adding dilute sulphuric acid to tartar-emetic (see below). It is insoluble, and easily loses water, giving the trioxide.

The trioxide interacts with potassium and sodium hydroxides, forming soluble **antimonites**, but the latter are much hydrolyzed by water, and cannot be isolated in solid form.

Salts of Antimony. — The **nitrate** $Sb(NO_3)_3$ and the **sulphate** $Sb_2(SO_4)_3$ are made by the interaction of the trioxide with nitric and sulphuric acids. They are hydrolyzed by water, giving basic salts, such as $(SbO)_2SO_4$ ($= Sb_2O_2SO_4$), which, like SbOCl, are derived from the hydroxide SbO(OH). When the trioxide is heated with a solution of potassium bitartrate $KHC_4H_4O_6$, a basic salt $K(SbO)C_4H_4O_6$, known as **tartar-emetic**, is formed. This is a white, crystalline substance which is soluble in water and is used in medicine. The univalent group SbO^1 is known as **antimonyl**, and the above mentioned basic compounds are often called antimonyl sulphate, etc.

Antimonic Acid. — By vigorous oxidation of antimony with nitric acid, or by decomposing the pentachloride completely with water, a white, insoluble substance of the approximate composition H_3SbO_4 is obtained. This substance interacts with caustic potash and passes into solution. But the salts which have been made are pyro- and metantimoniates. Thus, when antimony is fused with niter, **potassium metantimoniate** $KSbO_3$ is formed. When dissolved, this salt takes up water, and forms a solution of the acid pyroantimoniate:

$$2KSbO_3 + H_2O \rightarrow K_2H_2Sb_2O_7.$$

If this is added to a strong solution of a salt of sodium, a **sodium pyroantimoniate** is thrown down, $Na_2H_2Sb_2O_7$. The same insoluble body, almost the only salt of sodium which deserves this name, is formed also by direct action of sodium hydroxide upon antimonic acid.

Sulphides of Antimony. — There are two sulphides, the trisulphide Sb_2S_3 and the pentasulphide Sb_2S_5. The **trisulphide** is found in nature as the black, crystalline stibnite. By the action of hydrogen

sulphide upon solutions of salts of antimony, the trisulphide is precipitated as an orange-red powder, which, however, after having been melted, assumes the appearance of stibnite:

$$2SbCl_3 + 3H_2S \rightleftarrows Sb_2S_3 \downarrow + 6HCl.$$

The antimony trisulphide is decomposed, and the above action is reversed, by concentrated hydrochloric acid. Like cadmium sulphide, this substance is formed only when the acid present is dilute.

The **pentasulphide** is obtained by the decomposition of sulphantimoniates (see below). In appearance it resembles the trisulphide and, when heated, it decomposes very readily into this substance and free sulphur. It is used for vulcanizing rubber.

Sulphantimonites and Sulphantimoniates. — The behavior of the sulphides of antimony towards solutions of the alkali sulphides is very similar to that of the sulphides of arsenic (p. 712). The trisulphide dissolves in colorless ammonium sulphide with difficulty, forming an unstable ammonium sulphantimonite:

$$Sb_2S_3 + 3(NH_4)_2S \rightarrow 2(NH_4)_3SbS_3.$$

With the pentasulphide or with yellow ammonium sulphide the action takes place more readily and ammonium sulphantimoniate is formed:

$$Sb_2S_5 + 3(NH_4)_2S \rightarrow 2(NH_4)_3SbS_4,$$
$$Sb_2S_3 + 3(NH_4)_2S + 2S \rightarrow 2(NH_4)_3SbS_4.$$

The most familiar substance of this class is Schlippe's salt Na_3SbS_4, $9H_2O$. Pyrargyrite Ag_3SbS_3 (p. 626) is a native sulphantimoniate.

When acids are added to solutions of sulphantimoniates, the sulphantimonic acid which is liberated decomposes, and antimony pentasulphide is thrown down (see under Arsenic, p. 713).

BISMUTH.

The Chemical Relations of the Element. — Bismuth forms no compound with hydrogen. Its compounds with the halogens are of the form BiX_3 and are hydrolyzed by water giving basic salts. The oxide Bi_2O_3 is basic, and, although an oxide Bi_2O_5 is known, it is not acidic. Bismuth gives a carbonate, nitrate, sulphate, phosphate, and other salts, in all of which it acts as a trivalent element. It forms no soluble complex sulphides.

Occurrence and Physical Properties. — This element is found free in nature, and also to some extent as trioxide Bi_2O_3 and trisulphide Bi_2S_3. It is a shining, brittle metal with a reddish tinge. It melts at about 270°. When converted into vapor, its density at 1600–1700° is somewhat less than that corresponding to the formula Bi_2.

Mixtures of bismuth with other metals of low melting-point fuse at lower temperatures than do the separate metals. This is another illustration of the fact that a solution melts at a lower temperature than the pure solvent (p. 532). Thus, Wood's metal, containing bismuth (m.-p. 270°) 4 parts, lead (m.-p. 326°) 2 parts, tin (m.-p. 233°) 1 part, and cadmium (m.-p. 320°) 1 part, melts at 60.5°, considerably below the boiling-point of water. Similar alloys are used for safety plugs in steam-boilers, and, in the chemical laboratory, for filling baths in which a uniform temperature higher than 100° is to be maintained.

Chemical Properties. — Bismuth does not tarnish, but when heated strongly in the air it burns to form the trioxide. With the halogens it forms a fluoride, a bromide, and an iodide, in all of which the element is trivalent. When the metal is treated with oxygen acids, or the trioxide with any acids, salts are produced.

Oxides. — In addition to the basic trioxide, which is a yellow powder obtained by direct oxidation of the metal or by ignition of the nitrate, three other oxides are known — BiO, Bi_2O_4, and Bi_2O_5. None of these, however, is acid-forming, or gives corresponding salts when treated with acids.

Salts of Bismuth. — The salts of bismuth, when dissolved in water, are decomposed in a manner which recalls the behavior of the compounds of antimony. The products are insoluble basic salts, and the actions are reversible, the basic salts being redissolved by addition of an excess of the acid. In the case of the **chloride** $BiCl_3, H_2O$ and the **nitrate** $Bi(NO_3)_3, 5H_2O$, the actions taking place are:

$$BiCl_3 + 2H_2O \rightleftarrows Bi(OH)_2Cl + 2HCl,$$
$$Bi(NO_3)_3 + 2H_2O \rightarrow Bi(OH)_2NO_3 + 2HNO_3.$$

The former of these products, when dried, loses a molecule of water, giving the **oxychloride** $BiOCl$. The **oxynitrate** of bismuth is much used in medicine under the name of "subnitrate of bismuth."

It will be seen that, although bismuth forms a colorless ion $Bi^{\cdot\cdot\cdot}$, and is in this respect a metal in the chemical sense of the term, yet, like many other metals, it is related to the non-metals inasmuch as its salts are at least partially hydrolyzed by water.

Bismuth forms a **trisulphide** Bi_2S_3, which may be obtained by direct union of the elements, or by the action of hydrogen sulphide upon solutions of bismuth salts :

$$2BiCl_3 + 3H_2S \rightleftarrows Bi_2S_3\downarrow + 6HCl.$$

It is a brownish-black, insoluble substance, but on addition of much acid the above action is reversed. This sulphide is not affected by solutions of ammonium sulphide or of potassium sulphide. It differs, therefore, markedly from the sulphides of arsenic and antimony in its behavior.

The Family as a Whole.

When we compare the elements of this group, taking nitrogen as the first of the family in spite of the fact that it is somewhat less closely related to the other members than they are to one another, we find an admirable illustration of the general principles which the periodic system presents.

The elements themselves change progressively in physical properties as the atomic weight increases. Nitrogen is a gas which with sufficient cooling yields a white solid, phosphorus an almost white, or a red solid, and arsenic, antimony, and bismuth are metallic in appearance. The first combines directly with hydrogen, the next three give hydrides indirectly, and the last does not unite with hydrogen at all. The hydride of nitrogen combines with water to form a base, while the other hydrides show no such tendency. Ammonia unites with all acids, including those of the halogens, to form salts; phosphine with the hydrogen halides only; the others do not combine with acids at all. As regards their metallic properties, in the chemical sense, nitrogen and phosphorus do not by themselves form positive ions, and furnish us therefore with no salts whatever. Arsenic gives a trivalent positive ion, which is found in solutions of the halides only. It forms no normal sulphates, nitrates, or other salts. Antimony and bismuth both give trivalent positive ions. The sulphates, nitrates, etc., of antimony, however, are readily decomposed by water with precipitation of the hydroxide. The salts of bismuth,

on the other hand, do not readily give the pure hydroxide with water, although they are easily hydrolyzed to basic salts.

The halogen compounds of nitrogen and phosphorus are completely hydrolyzed by water, and do not exist when any water is present, even when excess of the halogen acid is used. The halogen compounds of arsenic are completely hydrolyzed by cold water, but exist in solution in presence of excess of the acids. The halogen compounds of antimony and bismuth are incompletely hydrolyzed by cold water.

Nitrogen forms five different oxides, a larger number than that furnished by any of the other elements of this group. The oxides upon which we naturally fix our attention are the trioxide and pentoxide in each case. With nitrogen these are acid-forming, being the anhydrides of nitric and nitrous acids. With phosphorus the trioxide and the pentoxide are anhydrides of acids. With arsenic the trioxide is basic towards the halogen acids, and is the first example of a basic oxide which we encounter in this group. The pentoxide, however, is acid-forming. The trioxide of antimony is mainly base-forming, although it is feebly acid-forming also. The pentoxide is acid-forming. The trioxide of bismuth is base-forming exclusively, and the pentoxide has no derivatives.

If the chemical actions which these elements and their compounds undergo were examined more closely, this progressive change in the properties with change in atomic weight could be developed much further. We have said sufficient, however, to show that when the periodic law is borne in mind it furnishes valuable aid in systematizing the chemistry of a group like this.

Analytical Reactions of Arsenic, Antimony, and Bismuth. — The ions which are most frequently encountered are $As^{\cdot\cdot\cdot}$, $Sb^{\cdot\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$, AsO_4''', and AsO_3'''. The first three, with hydrogen sulphide, give colored sulphides which are not affected by dilute acids. The sulphides of arsenic and antimony are separable from the sulphide of bismuth by solution in yellow ammonium sulphide. The ion of the arsenates AsO_4''' is identified by its interaction with salts of silver and the formation of $MgNH_4AsO_4$, while that of the arsenites AsO_3''' is recognized by its reducing power. By means of Marsh's test and the facts described under it (p. 714), the presence of traces of compounds of arsenic and antimony may be recognized and the elements may be distinguished. Oxygen compounds of arsenic, when heated with carbon, give a volatile, metallic-looking deposit of arsenic.

Vanadium, Columbium, Tantalum.

Of these elements, **vanadium** is less uncommon than the others. It is found in rather complex compounds. When these are heated with soda and sodium nitrate, **sodium vanadate** is formed, and can be extracted with water. Solid ammonium chloride is added to the solution, and ammonium metavanadate NH_4VO_3, which is less soluble in solutions of salts of ammonium (*cf.* p. 584) than in water, appears in the form of yellow crystals. When this salt is heated, **vanadic anhydride** V_2O_5, a yellowish-red powder, remains. This oxide interacts with bases giving vanadates, of which the most stable are the metavanadates. The element forms several **chlorides**, such as VCl_2, VCl_3, VCl_4, $VOCl_3$, and five **oxides**, V_2O, VO, V_2O_3, VO_2, and V_2O_5. The element has very feeble base-forming properties, and gives only a few unstable salts.

Columbium (or niobium) and **tantalum** likewise possess feebly base-forming properties, their chief compounds being the columbates and tantalates.

Exercises. — 1. How do you account for the fact that the molecular weight of arsenic at 644° is not exactly 300, and why is 308.4 ÷ 4 not accepted as the atomic weight? Could the atomic weight be found from the determination of the vapor density of the free element alone?

2. What should you expect to be the interaction of arsine with concentrated nitric acid?

3. Formulate the series of changes involved in the solution of arsenic trioxide and the interaction of hydrochloric acid with the arsenious acid so formed (*cf.* p. 371).

4. What is the full significance of the fact that arsenic pentasulphide may be precipitated by hydrogen sulphide from a solution of arsenic acid in hydrochloric acid?

5. To what classes of chemical changes do the interactions of arsenious sulphide and antimony trisulphide with yellow ammonium sulphide belong?

6. Construct equations showing the interaction of (*a*) concentrated sulphuric acid and antimony, (*b*) arsenic and bleaching-powder solution, (*c*) antimony and yellow ammonium sulphide, (*d*) silver nitrate and stibine, (*e*) silver nitrate and arsine, (*f*) concentrated nitric acid and antimony, (*g*) acids and ammonium orthosulphantimoniate.

7. How should you set about making Schlippe's salt?

keep the mass porous and accessible to the oxygen of the air, the potassium compounds being easily fusible:

$$4Fe(CrO_2)_2 + 8K_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2.$$

The iron is oxidized to ferric oxide, and the chromium passes from the state of chromic oxide in the chromite (FeO,Cr_2O_3) to that of chromic anhydride in the potassium chromate (K_2O,CrO_3). Thus, more insight is given into the nature of the action by the equation

$$4(FeO,Cr_2O_3) + 8(K_2O,CO_2) + 7O_2 \rightarrow 2Fe_2O_3 + 8(K_2O,CrO_3) + 8CO_2.$$

The cinder is treated with hot potassium sulphate solution. This interacts with the calcium chromate, which is formed at the same time, giving insoluble calcium sulphate:

$$CaCrO_4 + K_2SO_4 \rightleftarrows CaSO_4 \downarrow + K_2CrO_4.$$

The whole of the potassium chromate goes into solution.

Potassium chromate is pale-yellow in color, rhombic in form (isomorphous with potassium sulphate), and is very soluble in water (61 : 100 at 10°).

Sodium chromate is made by using sodium carbonate in the process just described.

The Dichromates. — When a solution of potassium sulphate is mixed with an equivalent amount of sulphuric acid, potassium bisulphate is obtainable by evaporation: $K_2SO_4 + H_2SO_4 \rightarrow 2KHSO_4$. The dry acid salt, when heated, loses water (p. 388), giving the pyrosulphate (or disulphate): $2KHSO_4 \rightleftarrows K_2S_2O_7 + H_2O$, but the latter, when redissolved, returns to the condition of acid sulphate. Now, when an acid is added to a chromate we should expect the chromic acid H_2CrO_4, thus liberated, to interact, giving an acid chromate (say, $KHCrO_4$). No acid chromates are known, however, and instead of them, pyrochromates or dichromates are produced, with elimination of water. In other words, the second of the above actions is not appreciably reversible when chromates are in question:

$$\begin{array}{lll} K_2CrO_4 + H_2SO_4 & \rightarrow (H_2CrO_4) + K_2SO_4 & \\ K_2CrO_4\,(+ H_2CrO_4) & \rightarrow K_2Cr_2O_7 + H_2O & \\ \hline 2K_2CrO_4 + H_2SO_4 & \rightarrow K_2Cr_2O_7 + H_2O + K_2SO_4 & \quad (1) \end{array}$$

In terms of the ionic hypothesis, S_2O_7'' is unstable in water, and interacts with it, giving hydrion and sulphanion, while Cr_2O_7'' is stable in water and is formed from the interaction of hydrion and chromanion:

$$S_2O_7'' + H_2O \leftrightarrows 2H^{\cdot} + 2SO_4'',$$
$$Cr_2O_7'' + H_2O \leftrightarrows 2H^{\cdot} + 2CrO_4''. \qquad (2)$$

The dichromates of potassium and sodium are made by adding sulphuric acid to the crude solution of the chromate obtained from chromite (p. 724). They crystallize when the liquid cools, and the mother-liquor, containing the potassium sulphate and undeposited dichromate, is used for extracting a fresh portion of cinder. As the dichromates are much less soluble than the chromates, they crystallize from less concentrated solutions, and can therefore be obtained in purer condition. For this reason the extract is always treated for dichromate.

Potassium dichromate $K_2Cr_2O_7$ (or K_2CrO_4,CrO_3) crystallizes in asymmetric tables of orange-red color. Its solubility in water is 8 : 100 at 10° and 12.5 : 100 at 20°. **Sodium dichromate** $Na_2Cr_2O_7,2H_2O$ forms red crystals also, and its solubility is 109 : 100 at 15°. This salt is now cheaper than potassium dichromate, and has largely displaced the latter for commercial purposes.

By treatment of the chromates with larger amounts of free acid, other polychromates are formed. Thus, with increasing amounts of nitric acid, ammonium chromate gives first the dichromate $(NH_4)_2Cr_2O_7$, which may be written $(NH_4)_2CrO_4,CrO_3$, then the trichromate $(NH_4)_2CrO_4,2CrO_3$, and even the tetrachromate $(NH_4)_2CrO_4,3CrO_3$, all of which are red crystalline substances.

Chemical Properties of the Dichromates. — 1. When concentrated sulphuric acid is added to a strong solution of a dichromate (or chromate), chromic anhydride separates in red needles:

$$Na_2Cr_2O_7 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + 2CrO_3.$$

2. Although a dichromate lacks the hydrogen, it is essentially of the nature of an acid salt, just as SbOCl lacks hydroxyl, but is essentially a basic salt. Hence, when potassium hydroxide is added to a solution of potassium dichromate, potassium chromate is formed:

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O.$$

The solution changes from red to yellow, and the chromate is obtained by evaporation. It is in this way that pure alkali chromates are made.

3. By addition of potassium dichromate to a solution of a salt of a metal whose chromate is insoluble, the chromate and not the dichromate is precipitated. This is in consequence of the fact that there is always a little hydrion and CrO_4'' (equation (2) above) in the solution of the dichromate:

$$2Ba(NO_3)_2 + K_2Cr_2O_7 + H_2O \rightleftarrows 2BaCrO_4\downarrow + 2KNO_3 + 2HNO_3.$$

Being essentially an acid salt, the dichromate produces a salt and an acid, as any acid salt would do. For example:

$$Ba(NO_3)_2 + KHSO_4 \rightleftarrows BaSO_4\downarrow + KNO_3 + HNO_3.$$

Soluble chromates are, naturally, equally good precipitants of insoluble ones.

4. The dichromates of potassium and sodium melt when heated, and, at a white heat, decompose, giving the chromate, chromic oxide, and free oxygen. To make the equation, we note that the dichromate, for example $K_2Cr_2O_7$, consists of $K_2CrO_4 + CrO_3$, and the latter, if alone, will decompose thus: $2CrO_3 \rightarrow Cr_2O_3 + 3O$. Since the product must contain a multiple of O_2, the equation is:

$$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2.$$

5. With free acids the dichromates give powerful oxidizing mixtures, in consequence of their tendency to form chromic salts. Since the latter correspond to the oxide Cr_2O_3 and the former to CrO_3, the passage from the former to the latter must furnish 3O for every $2CrO_3$ transformed. In dilute solutions, unless a body capable of being oxidized is present, no actual decomposition, beyond the liberation of chromic acid * occurs. When concentrated hydrochloric acid is used, this acid itself suffers oxidation:

$$\begin{array}{l} K_2Cr_2O_7 + 8HCl \rightarrow 2KCl + 2CrCl_3 + 4H_2O\ (+ 3O) \\ (3O) \quad + 6HCl \rightarrow 3H_2O + 3Cl_2 \\ \hline K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2 \end{array}$$

When sulphuric acid is employed, an oxidizable substance such as

* Not shown as a distinct stage in the subsequent equations.

hydrogen sulphide (*cf.* p. 374), sulphurous acid, or alcohol must be present:

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O\ (+\ 3O) \quad (1)$$

$$(3O) + 3H_2SO_3 \rightarrow 3H_2SO_4 \quad (2)$$

or

$$(3O) + \underset{[alcohol]}{3C_2H_5OH} \rightarrow \underset{[aldehyde]}{3C_2H_4O} \uparrow + 3H_2O \quad (2')$$

In each case the usual summation of (1) and (2), with omission of the 3O gives the equation for the whole action. When (1) is dissected, $K_2O, 2CrO_3$ giving $3SO_3, Cr_2O_3 + 3O$ is found to be its essential content. In practice, this sort of action is used for the purpose of making chromic salts, and for its oxidizing effects, as in the preparation of aldehyde and in the dichromate battery (*q.v.*).

6. When a body which is not merely oxidizable, but is an active reducing agent, is employed, the dichromate may be reduced without the addition of any acid. For example, when warmed with ammonium sulphide, a dichromate gives chromic hydroxide and free sulphur:

$$K_2Cr_2O_7 + 3(NH_4)_2S + 7H_2O \rightarrow 2Cr(OH)_3 + 3S + 2KOH + 6NH_4OH.$$

If the reducing body is less active, the change may nevertheless take place under the influence of light. Thus, when paper is coated with gelatine containing a soluble chromate or dichromate, and, after being dried, is exposed to light, chromic oxide is formed by reduction, and combines with the gelatine to give an organic compound. This product will not swell up or dissolve in tepid water as does pure gelatine. This action is used in many ways for purposes of artistic reproduction. Thus, if the gelatine mixture is made up with lampblack, and, after the coating has dried, is covered with a negative and exposed to light, the parts which were protected from illumination may afterwards be washed away, while the "carbon print" remains. The gelatine layer can be transferred to wood or copper before washing. When materials of different colors are substituted for the lampblack, prints of any desired tint may be made by the same process.

Insoluble Chromates. — A number of chromates, formed by precipitation with a solution of a soluble chromate or dichromate, are familiar. Thus, **lead chromate** $PbCrO_4$ is used as a yellow pigment. By treatment with lime-water it gives a basic salt of brilliant red color — "chrome-red" Pb_2OCrO_4. Salts of calcium give a yellow, hydrated **calcium chromate** $CaCrO_4, 2HO_2$ analogous to gypsum, and, like it, per-

ceptibly soluble in water (0.4 : 100 at 14°). **Barium chromate** $BaCrO_4$ is also yellow. Being a salt of a feeble acid, it interacts with active acids, and passes into solution. Like calcium oxalate (*cf.* p. 599), it is not soluble enough to be attacked by acetic acid. **Strontium chromate**, however, is soluble in acetic acid. **Silver chromate** is red, and interacts easily with acids. It will be observed that there is a close correspondence between the relative solubilities of the chromates and the sulphates.

Chromyl Chloride. — This compound corresponds to sulphuryl chloride SO_2Cl_2, and is made by distilling a dichromate with a chloride and concentrated sulphuric acid:

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 + 3K_2SO_4 + 3H_2O.$$

The hydrochloric acid liberated from the chloride may be supposed to interact with chromic acid from the dichromate:

$$CrO_2(OH)_2 + 2HCl \rightarrow CrO_2Cl_2 + 2H_2O.$$

Chromyl chloride is a red liquid, boiling at 118°. It fumes strongly in moist air, being hydrolyzed by water. This action is the reverse of that shown in the last equation. No corresponding bromine and iodine compounds are known; and when a bromide or iodide is treated as described above, the halogens are liberated by oxidation, and no volatile compound of chromium appears. Hence, when an unknown halide is mixed with potassium dichromate and sulphuric acid and distilled, and the vapors are caught in ammonium hydroxide, the finding of a chromate in the distillate demonstrates the existence of a chloride in the original substance:

$$CrO_2Cl_2 + 4NH_4OH \rightarrow (NH_4)_2CrO_4 + 2NH_4Cl + 2H_2O.$$

This action is used as a test for the presence of traces of chlorides in large amounts of bromides or iodides.

Chromic Anhydride. — The oxide CrO_3 is made as described above (par. 1, p. 725), and is often called chromic acid. It is soluble in water, and combines with the latter to some extent, giving dichromic acid $H_2Cr_2O_7$. In acidified solution it is much used as an oxidizing agent for organic substances. It interacts with acids in the same way as do the dichromates, giving chromic salts and furnishing oxygen to

the oxidizable body. When heated by itself, it loses oxygen readily, and yields the green chromic oxide: $4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2$.

Perchromic Acid. — When hydrogen peroxide (*cf.* p. 306) is present in solution with free chromic acid, a deep-blue, unstable compound is formed. It can be extracted from the solution by means of ether, and its formation is used as a delicate test for hydrogen peroxide (*q.v.*). It is supposed to be a mixed anhydride of hydrogen peroxide with dichromic acid, perhaps $H_2Cr_2O_8$ (*cf.* p. 397).

Chromic Compounds.

Chromic Chloride. — A hydrated chloride $CrCl_3, 6H_2O$ is obtained by treating the hydroxide $Cr(OH)_3$ with hydrochloric acid and evaporating. When heated, this is hydrolyzed, and chromic oxide remains. The anhydrous chloride is formed by sublimation, as a mass of brilliant, reddish-violet scales, when chlorine is led over a heated mixture of chromic oxide and carbon (*cf.* Silicon tetrachloride):

$$Cr_2O_3 + 3C + 3Cl_2 \rightarrow 2CrCl_3 + 3CO.$$

In this form the substance dissolves with extreme slowness, even in boiling water, but in presence of a trace of chromous chloride or stannous chloride it is easily soluble. The solution is green, as are all solutions of chromic salts after they have been boiled, but on standing in the cold, blue crystals of $CrCl_3, 6H_2O$ are deposited. These give a blue solution containing $Cr^{\cdot\cdot\cdot} + 3Cl'$, but boiling reproduces the green color. The green material is a basic salt of an exceptional nature. It has lost one unit of chlorine by hydrolysis, and one of the two others is not precipitated by nitrate of silver. The substance is supposed, therefore, to contain a complex cation and to have the formula $CrClOH.Cl$.

Chromic Hydroxide. — When ammonium hydroxide is added to a solution of a chromic salt, a hydrated hydroxide of pale-blue color, $Cr(OH)_3, 2H_2O$, is thrown down. This loses water by stages, giving intermediate hydroxides such as $Cr(OH)_3$ and $CrOOH$, and finally Cr_2O_3. It interacts with acids, giving chromic salts. It also dissolves in potassium and sodium hydroxides to form green solutions of **chromites** of the form $KCrO_2$. When the solutions of the alkali chromites are boiled, the free hydroxide, present in consequence of

hydrolysis, is converted into a greenish, less completely hydrated, and less soluble variety. This begins to come out as a precipitate, and soon the whole action is reversed. Insoluble chromites, such as that of iron $Fe(CrO_2)_2$, are found in nature. Many of them, like $Zn(CrO_2)_2$ and $Mg(CrO_2)_2$, may be formed by fusing the oxide of the metal with chromic oxide; the action being similar to that used in making zincates (p. 648) and aluminates (p. 691).

Chromic Oxide. — This oxide is obtained as a green, infusible powder by heating the hydroxide; or, more readily, by heating dry ammonium dichromate; or by igniting potassium dichromate with sulphur and washing the potassium sulphate out of the residue:

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3,$$
$$K_2Cr_2O_7 + S \rightarrow K_2SO_4 + Cr_2O_3.$$

Chromic oxide is not affected by acids, but may be converted into the sulphate by fusion with potassium bisulphate. It is used for making green paint, and for giving a green tint to glass. When the oxide, or any of the chromic salts, is fused with a basic substance such as an alkali carbonate, it passes into the form of a chromate, absorbing the necessary oxygen from the air. If an alkali nitrate or chlorate is added, the oxidation goes on more quickly. The alkaline solution of the chromites may be oxidized, for example, by addition of chlorine or bromine, and chromates are formed.

Chromic Sulphate. — This salt crystallizes in reddish-violet crystals of a hydrate $Cr_2(SO_4)_3,15H_2O$, and may be made by treating the hydroxide with sulphuric acid. It gives reddish-violet, octahedral crystals of **chrome-alum** (*cf.* p. 687), $K_2SO_4, Cr_2(SO_4)_3, 24H_2O$, when mixed with potassium sulphate. This double salt is most easily obtained by reducing potassium dichromate in dilute sulphuric acid by means of sulphurous acid (p. 727), and allowing the solution to crystallize. The solution of the crystals, either of the pure sulphate or of the alum, is bluish-violet ($Cr^{\cdot\cdot\cdot}$), but when boiled becomes green. The green compound is formed by hydrolysis and is gummy and uncrystallizable. It even yields products which do not show the presence either of the $Cr^{\cdot\cdot\cdot}$ or the SO_4'' ion. It seems to be formed thus:

$$2Cr_2(SO_4)_3 + H_2O \rightleftarrows Cr_4O(SO_4)_4.SO_4 + H_2SO_4.$$

The green materials revert slowly to the violet ones by reversal of the above action when the solution remains in the cold, and so crystals of the sulphate or of the alum are obtainable from the green solutions.

Chromic Acetate. —This salt, $Cr(C_2H_3O_2)_3$, is made by treating the hydroxide with acetic acid, and a green solution of it is used as a mordant by calico-printers (*cf.* p. 689).

CHROMOUS COMPOUNDS.

By the interaction of chromium with hydrochloric acid, or by reducing chromic chloride in a stream of hydrogen, **chromous chloride** $CrCl_2$ is formed. The anhydrous salt is colorless, and its solution is blue ($Cr^{\cdot\cdot}$). Like stannous chloride, it is very easily oxidized by the air, a solution of it containing excess of hydrochloric acid being used in the laboratory to absorb oxygen:

$$4CrCl_2 + 4HCl + O_2 \rightarrow 4CrCl_3 + 2H_2O.$$

Chromous hydroxide is obtained as a yellow precipitate when alkalies are added to the chloride. With sulphuric acid it gives **chromous sulphate** $CrSO_4, 7H_2O$, which is isomorphous with the vitriols (p. 649).

Chromous salts give with ammonium sulphide a black precipitate of **chromous sulphide**, and with sodium acetate a red precipitate of **chromous acetate**. The latter is not very soluble, and is less quickly oxidized by the air than any of the other chromous compounds.

Analytical Reactions of Chromium Compounds. — The chromic salts give the bluish-violet trichromion $Cr^{\cdot\cdot\cdot}$, or the green complex cations, and may be recognized in solution by their color. The chromates and dichromates give the ions CrO_4'' and Cr_2O_7'', which are yellow and red respectively. From chromic salts, alkalies and ammonium sulphide precipitate the bluish-green hydroxide, and carbonates give a basic carbonate which is almost completely hydrolyzed to hydroxide. By fusion with sodium carbonate and sodium nitrate, they yield a yellow bead containing the chromate. The chromates and dichromates are recognized by the insoluble chromates which they precipitate, and by their oxidizing power when mixed with acids. All compounds of chromium give a green borax bead containing chromic borate, and this bead differs from that given by compounds of copper (*cf.* p. 626), which is also green, in being unreducible.

Molybdenum, Tungsten, Uranium.

As was stated at the opening of the chapter, these elements give acid anhydrides of the form XO_3, and acids and salts of the form H_2XO_4. They also give salts of the form $H_2X_2O_7$ corresponding to the dichromates. Uranium has base-forming properties as well.

Molybdenum. — This element is found chiefly in wulfenite $PbMoO_4$ and molybdenite MoS_2. The latter resembles black lead (graphite), and its appearance suggested the name of the element (Gk. μολύβδαινα, lead). The molybdenite is converted by roasting into **molybdic anhydride** MoO_3. When this is treated with ammonium hydroxide, or with sodium hydroxide, **ammonium molybdate** $(NH_4)_2MoO_4$, or **sodium molybdate** $Na_2MoO_4, 10H_2O$ is obtained. The **metal** itself is liberated by reducing the oxide or chloride with hydrogen. When pure it resembles wrought iron, and, like iron (*q.v.*), takes up carbon and shows the phenomena of tempering. The **oxides** [MoO ?], Mo_2O_3, MoO_2, and MoO_3 are known, but the lower oxides are not basic. The **chlorides** Mo_3Cl_6, $MoCl_3$, $MoCl_4$, and $MoCl_5$ have been made. The chief use of molybdenum compounds in the laboratory is in **testing for** and estimating **phosphoric acid**. When a little of a phosphate is added to a solution of ammonium molybdate in nitric acid, and the mixture is warmed, a copious yellow precipitate of a **phosphomolybdate of ammonium** $(NH_4)_3PO_4, 11MoO_3, 6H_2O$ is formed. The compound is soluble in excess of phosphoric acid and in alkalies, but not in dilute mineral acids.

Tungsten. — The minerals scheelite $CaWO_4$ and wolfram $FeWO_4$ are tungstates of calcium and iron respectively. By fusion of wolfram with sodium carbonate and extraction with water, **sodium tungstate** $Na_2WO_4, 2H_2O$ is secured. It is used as a mordant and for rendering muslin fire-proof. Acids precipitate **tungstic acid** H_2WO_4, H_2O from solutions of this salt. The element gives the **oxides** WO_2 and WO_3, the latter being formed by ignition of tungstic acid. The **chlorides** WCl_2, WCl_4, WCl_5, and WCl_6 are known, the last being formed directly, and the others by reduction. A hard variety of steel contains 5 per cent of tungsten.

Uranium. — This element is found chiefly in pitchblende, which contains the oxide U_3O_8 along with smaller amounts of many other ele-

ments. By roasting the ore with carbonate and nitrate of sodium, and extracting with water, an impure solution of **sodium uranate** $NaUO_4$ is obtained. Acids precipitate the insoluble, yellow **diuranate** $Na_2U_2O_7$, $6H_2O$. This salt is used in making **uranium glass**, which shows a yellowish-green fluorescence. The property is due to the fact that the wave-length of part of the invisible, ultra-violet rays of the sunlight are shortened, and a greenish light is therefore in excess. The **oxides** are UO_2 a basic oxide, U_2O_5, U_3O_8 the most stable oxide, UO_3 uranic anhydride, and UO_4 a peroxide.

When the oxide UO_2 is treated with acids, it gives **uranous salts** such as uranous sulphate $U(SO_4)_2, 4H_2O$. Uranic anhydride and uranic acid interact with acids, giving basic salts, such as UO_2SO_4, $3\frac{1}{2}H_2O$, and $UO_2(NO_3)_2, 6H_2O$, which are named **uranyl sulphate**, uranyl nitrate, and so forth. They are yellow in color, with green fluorescence. Ammonium sulphide throws down the brown, unstable uranyl sulphide UO_2S from their solutions.

Radium.

The Discovery of the Element.* — It was Becquerel who first noticed (1898) that all compounds of uranium gave out a radiation capable of affecting a photographic plate covered with black, light-proof paper. The Becquerel rays, however, required several days to produce a distinct effect. These rays had a second, equally remarkable property. Ordinary air is an extremely poor conductor of electricity, and for this reason a well-insulated, electrically charged body, such as an electroscope, will retain its charge for a long time. Yet a few tenths of a gram of any uranium compound, brought within 3 or 4 cm. of the charged body, rendered the air a conductor, and the charge was quickly lost. The air, under these conditions, is said to be "ionized," but the positive and negative ions it contains are probably large molecular complexes. This property makes possible the quantitative measurement of radio-activity, or the rate of production of Becquerel rays. We simply have to compare the times required for the discharge of an electroscope by different specimens of radio-active matter.

The radio-activity of every pure uranium compound is proportional to its uranium content. The ores are, however, relatively four times as active. This fact led M. and Mme. Curie to the discovery that the

* I am indebted to my colleague Professor H. N. McCoy for the material of which the following is a slightly condensed version.

pitchblende residues, from which practically all of the uranium had been extracted, were nevertheless quite active. About a ton of the very complex residues having been separated laboriously into the constituents, it was found that a large part of the radio-activity remained with the compound of barium. The barium chloride, after being purified until no other elements could be detected in it by ordinary chemical tests, was sixty times as active as uranium. The percentage of chlorine contained in it was almost identical with that in the ordinary salt, and it differed from this only in its photo-active and "ionizing" powers. By repeated systematic recrystallization, however, a portion was separated which gave distinctly the spectrum of a new element and a diminished percentage of chlorine. Finally, a product free from barium, and three million times as active as uranium, was secured. The nature of the spectrum and the chemical relations of the element, now named **radium**, placed it with the metals of the alkaline earths. The ratio by weight of chlorine to radium in the compound was 35.45 : 112.5, so that, on the assumption that the element is bivalent, its atomic weight is 225. With this value it occupies a place formerly vacant in the periodic table.

Properties of Radium Compounds. — Radium has not been isolated, and the chloride and bromide are usually employed. The enormous photo-activity and ionizing power of the compound has been mentioned above. The rays, like X-rays, may cause severe "burns." Many substances, like zinc-blende and the diamond, phosphoresce brilliantly when exposed to the rays. The most remarkable property of the salts, however, is their constant evolution of heat in relatively enormous quantities. One gram of the element, in combination, evolves over 100 cal. per hour, and it is estimated that the total amount of heat spontaneously produced by 1 g. would be about 10^{10} cal. To produce the same amount of heat by combustion, no less than 300 kg. of hydrogen would have to be burned.

The Radiations of Radium Salts. — The Becquerel rays are made up of three different radiations: The α-rays, which produce the ionization, and are almost completely absorbed by a piece of paper; the β-rays, which produce the photographic effects and readily penetrate paper and even thin sheets of metal; the γ-rays, which resemble X-rays.

When ammonium carbonate is added in excess to a solution of a

soluble salt of uranium, a precipitate is formed and redissolves. A trifling undissolved residue, called uranium-X, however, possesses itself of all the β-ray activity of the original material. While the activity of any ordinary uranium compound is constant, that of U-X decreases rather rapidly, reaching half value in 22 days, and disappearing entirely in a few months.

The uranium freed from U-X has at first only α-ray activity, but after 22 days it has recovered half its former β-ray activity, and after a few months the whole. The removal of equal quantities of U-X may be repeated, in this way, at intervals of a few months, any number of times. There is thus a *continuous production of U-X from uranium.*

It has been found that the β-rays are identical with cathode rays, and, in terms of the molecular hypothesis, consist of minute particles, **electrons** or **corpuscles**, shot out with a velocity approaching that of light. The mass of each corpuscle is about $\frac{1}{1000}$ of that of an atom of hydrogen (*cf.* p. 222), and bears a negative charge of electricity equal to that on a chlorine ion in solution.

The α-rays consist of particles about twice as heavy as a hydrogen atom, and move with enormous velocity. Each of these particles bears a positive charge equal to that on one atom of hydrion.

Rutherford and Soddy account for the facts on which the above hypothetical statements are based by the **disintegration hypothesis.** All atoms are considered as groups of minute particles in a state of rapid orbital motion. The atoms of radio-active elements are not perfectly stable, and, occasionally, disintegration occurs, one or more of the particles being shot out. These particles constitute the α- and β-rays. The heating effect of radium salts is thus due to the change of the kinetic energy of the moving particles into heat when they encounter some other body.

The γ-rays probably originate by the impact of β-rays, just as X-rays are produced by cathode rays.

The Decay of an Element. — Uranium (at. wt. 238.5) has the heaviest known atom. The disintegration of its atom gives α-rays and leaves the lighter atoms of U-X. In a similar manner, radium gives rise to a new radio-active, gaseous body, the **radium emanation.** This, like U-X, is not permanent, and loses half its activity in four days. In doing so it produces a series of new radio-active substances. These, with their times of decay to half value, are as follows (Rutherford):

Ra →	Em →	A →	B →	C →	D →	E →	F
1500 yrs.	4 days	3 min.	26 min.	19 min.	40 yrs.	6 days	142 days

Radium thus loses its activity. To account for its presence in the ore, we must, therefore, suppose that it is being continuously produced from some source. This source must be uranium, for every known uranium ore contains radium (McCoy) and radium emanation (Boltwood) in amounts proportional to the uranium content. Furthermore, it is asserted by Soddy that the radium emanation is slowly re-formed in a uranium compound previously freed from radio-active substances, although Boltwood has failed to confirm this observation.

It has recently been found (Ramsay and Soddy) that helium (p. 430) is one of the decomposition products of the radium emanation.

The phenomena of radio-active substances lead undeniably to the startling conclusion that *some, if not all, of the elements are capable of spontaneous decomposition.* The transmutation of the elements, in the manner indicated, seems to be clearly established, since it appears certain that the element uranium produces another undoubted element, radium, which, in turn, yields the element helium. Besides the U – Ra series of radio-active substances, others are known. Thus, all of the compounds of thorium are radio-active, and other less well-characterized substances, such as polonium, actinium, radio-tellurium, radio-lead, etc., have been separated from pitchblende. It is probable that radio-lead is radium-D, and that radio-tellurium is radium-F. There is also considerable evidence that many other elements are very slightly radio-active, perhaps $\frac{1}{1000}$ as active as uranium. This may mean that all elements undergo an extremely slow, spontaneous decay. At present there is no known means of hastening the rate of radio-active change.

Exercises. — 1. Construct equations showing the interactions of (*a*) chromic oxide and aluminium, (*b*) strontium nitrate and potassium dichromate in solution, (*c*) potassium hydroxide and chromic hydroxide, and the reversal on boiling, (*d*) chlorine and potassium chromite in excess of alkali (what is the actual oxidizing agent ?).

2. What volume of oxygen at 0° and 760 mm. (*a*) is obtainable from one formula-weight of potassium dichromate (par. 4, p. 726), (*b*) is required to oxidize one formula-weight of chromous chloride ?

3. To what classes of actions should you assign the three methods of making chromic oxide (p. 730) ?

CHAPTER XLIII

MANGANESE

The Chemical Relations of the Element. — Manganese stands, at present, alone on the left side of the eighth column of the periodic table. The right side is occupied by the halogens. It is never univalent, as the halogens are, but its heptoxide Mn_2O_7 and the corresponding acid, permanganic acid $HMnO_4$, are in many ways closely related to the heptoxide of chlorine and perchloric acid $HClO_4$. Of the lower oxides of manganese, MnO is basic, and Mn_2O_3 feebly basic. MnO_2 is feebly acidic, MnO_3 more strongly so, and permanganic acid (from Mn_2O_7) is a very active acid. Contrary to the habit of feebly acidic and feebly basic oxides, such as those of zinc, aluminium, and tin, the basic oxides of manganese are not at all acidic, and the acidic oxides (with the possible exception of Mn_2O_3) are not also basic. There are thus the five following, rather well-defined sets of compounds, showing five different valences of the element. Of these the first, fourth, and fifth are the most stable and the most important.

1. **Manganous compounds**, MnO, $Mn(OH)_2$, $MnSO_4$, etc. These compounds resemble those of the magnesium family (and those of $Fe^{\cdot\cdot}$). The salts of weak acids, such as the carbonate and sulphide, are easily made, and there is little hydrolysis of the halides. The salts are pale-pink in color.

2. **Manganic compounds**, Mn_2O_3, $Mn(OH)_3$, $Mn_2(SO_4)_3$, $[MnCl_3]$. The salts resemble the chromic and aluminium salts in behavior, but are even less stable than those of quadrivalent lead. They are completely hydrolyzed by little water. The salts are violet in color.

3. **Manganites**, MnO_2, H_2MnO_3, $CaMnO_3$. The alkali manganites are strongly hydrolyzed, like plumbates and stannates.

4. **Manganates**, MnO_3, H_2MnO_4, K_2MnO_4. The salts resemble the sulphates and chromates, but are much more easily hydrolyzed. The free acid resembles chloric acid in that when it decomposes it yields a higher acid ($HMnO_4$) and a lower oxide (MnO_2). The salts are green in color.

5. **Permanganates**, Mn_2O_7, $HMnO_4$(hydrated), $KMnO_4$. The salts

resemble the perchlorates. and are not hydrolyzed by water. They are reddish-purple in color.

It will be seen that the element manganese changes its character totally with change in valence, and in each form of combination resembles some set of elements of valence identical with that which it has itself assumed.

Occurrence and Isolation. — The chief ore is the dioxide, pyrolusite MnO_2, which always contains compounds of iron. Other manganese minerals are: braunite Mn_2O_3; the hydrated form, manganite $MnO(OH)$; hausmannite Mn_3O_4; and manganese spar $MnCO_3$. The last is isomorphous with calcite. The metal is most easily made by reducing one of the oxides with aluminium by Goldschmidt's method.

Physical and Chemical Properties. — The metal manganese has a grayish luster faintly tinged with red. It rusts in moist air, and easily displaces hydrogen from dilute acids, giving manganous salts. Its alloys with iron, such as ferro-manganese (20–80 per cent manganese), are used in the arts.

Oxides. — **Manganous oxide** MnO is a green powder, made by reducing any of the other oxides with hydrogen. **Hausmannite** Mn_3O_4 is red. An oxide having this composition is formed when any of the other oxides is heated in air, oxidation or reduction, as the case may be, taking place (*cf.* p. 701). This oxide corresponds to minium Pb_3O_4 (p. 701) rather than to Fe_3O_4, for with dilute acids it gives a soluble manganous salt and a precipitate of the dioxide:

$$Mn_2MnO_4 + 4HNO_3 \rightarrow 2Mn(NO_3)_2 + H_4MnO_4\downarrow.$$

The hydrated dioxide H_4MnO_4 subsequently loses water. Hausmannite also forms square prismatic crystals. In view of its behavior with acids and its crystalline form, it is thought to be an orthomanganite of manganese Mn_2MnO_4, rather than a derivative of manganic oxide, $Mn(MnO_2)_2$, which would be a spinelle (p. 686). The magnetic oxide of iron $Fe(FeO_2)_2$ belongs to the regular system, like the spinelles. **Manganic oxide** Mn_2O_3 is brownish-black, and is formed by heating any of the oxides in oxygen. In dilute acids it behaves as if it were a manganite of manganese $Mn.MnO_3$, for it gives a manganous salt and manganese dioxide. Yet compounds of trivalent manganese are known, and this may be one.

Manganese dioxide MnO_2 is black, and is most easily prepared in pure condition by gentle ignition of manganous nitrate. The hydrated forms of the oxide are produced by reactions like those just mentioned, and by adding a hypochlorite or hypobromite to manganous hydroxide suspended in water. Manganese dioxide is not a peroxide in the restricted sense (*cf.* p. 308). It is used for manufacturing chlorine, although electrolytic processes are now driving it out of this field. In glass-making (*q.v.*), it is employed to oxidize the green ferrous silicate, derived from impurities in the sand, to the pale-yellow ferric compound. The amethyst color of the manganous silicate which is formed tends to neutralize this yellow. The dioxide forms the depolarizer in the Leclanché cell (p. 673).

Manganese trioxide is a red, unstable powder. **Manganese heptoxide** is a brownish-green oil (see below).

When any of these oxides is heated with an *acid*, a manganous salt is obtained. Salts of this class are, in fact, the only stable substances in which manganese is combined with an acid radical. In this action the oxides containing more oxygen than does MnO give off oxygen, or oxidize the acid (*cf.* p. 172). When the oxides are heated with *bases*, in the presence of air, manganates are always formed. With the oxides containing a smaller proportion of oxygen than MnO_3 oxygen is taken from the air.

Manganous Compounds. — The manganous salts are formed by the action of acids upon the carbonate or any of the oxides. Thus the **chloride** $MnCl_2, 4H_2O$ is obtained in pale-pink crystals from a solution made by treating the dioxide with hydrochloric acid and driving off the chlorine liberated by oxidation (p. 171). The **hydroxide** $Mn(OH)_2$ is formed as a white precipitate when a soluble base is added to a solution of a manganous salt. This body passes into solution when ammonium salts are added, and cannot be precipitated in their presence on account of the formation of molecular ammonium hydroxide and the suppression of hydroxidion (*cf.* magnesium hydroxide, p. 644). The hydroxide quickly darkens when exposed to the air and passes over into hydrated manganic oxide MnO(OH).

Manganous sulphate gives pink crystals of a hydrate. Below 6° the solution deposits $MnSO_4, 7H_2O$, which is a vitriol (p. 649). Between 7° and 20° the product is $MnSO_4, 5H_2O$, asymmetric and isomorphous with $CuSO_4, 5H_2O$. Above 25° monosymmetric prisms of $MnSO_4, 4H_2O$ are obtained. These hydrates have different aqueous

tensions and may be formed from one another by lowering or raising the pressure of water vapor around the substance (p. 122). The significance of the temperatures proper to the crystallization of each (*cf.* pp. 573, 608, 623) is that a given solid hydrate can be formed only in a solution which is saturated with respect to that hydrate and has the same aqueous tension as the hydrate. These conditions are necessary to that state of equilibrium between the solution and the hydrate on which the co-existence of solution and hydrate during crystallization depends (*cf.* p. 160). Hence the hydrates with the larger proportions of water, and the higher aqueous tensions, are formed in the colder solutions which contain less of the solute when saturated and have therefore at a given temperature themselves relatively high aqueous tensions.

The presence of a foreign dissolved body, since it will lower the vapor tension of the solution, may similarly cause the formation of a lower hydrate. Thus, at the ordinary temperature, calcium sulphate solution has a higher aqueous tension than gypsum, and therefore gypsum is deposited from it, and anhydrite will turn into gypsum if placed in it. But calcium sulphate solution containing much of the chlorides of sodium and magnesium has a lower aqueous tension than gypsum, and so anhydrite is deposited, and gypsum in contact with such a solution would lose its water of hydration. This explains the deposition of anhydrite in the salt layers (*cf.* p. 603).

Manganous carbonate $MnCO_3$ is a white powder formed by precipitation. The **sulphide** MnS is obtained as a green powder by leading hydrogen sulphide over any of the oxides. A flesh-colored, hydrated form MnS, H_2O is more familiar and is precipitated by ammonium sulphide from manganous salts. It interacts with mineral acids and even with acetic acid, so that it cannot be precipitated by hydrogen sulphide (*cf.* p. 651).

The manganous salts of weak acids, such as the carbonate and sulphide, darken when exposed to air and are oxidized, with formation of hydrated manganic oxide. As we have seen, manganous hydroxide is similarly oxidized and these salts are precisely the ones which should furnish the hydroxide by hydrolysis. While there is a general resemblance between the manganous salts and the stannous, chromous, and ferrous salts, the manganous salts of active acids are not oxidized by the air as are the corresponding salts of the other three metals.

Manganic Compounds. — The base of this set of compounds, **manganic hydroxide** $Mn(OH)_3$, is slowly deposited by the action of

the air on an ammoniacal solution of a manganous salt in salts of ammonium. The **chloride** $MnCl_3$ is present in the liquid obtained by the action of hydrochloric acid upon manganese dioxide (*cf.* p. 171), but loses chlorine very readily and cannot be isolated. Double salts such as $MnCl_3, 2KCl$ and $MnF_3, 2KF, 2H_2O$ are known. **Manganic sulphate** $Mn_2(SO_4)_3$ is deposited as a violet-red powder when hydrated manganese dioxide is heated with concentrated sulphuric acid at 160°. It is deliquescent and is rapidly hydrolyzed in the cold even by a little water, giving the brownish-black hydroxide:

$$Mn_2(SO_4)_3 + 6H_2O \rightarrow 2Mn(OH)_3 + 3H_2SO_4.$$

The **caesium-manganic alum** $Cs_2SO_4, Mn_2(SO_4)_3, 24H_2O$ seems to be the most stable derivative.

Manganites.—Although manganese dioxide interacts when fused with potassium hydroxide, simple salts derived from H_2MnO_3 ($= H_2O, MnO_2$) or H_4MnO_4 ($= 2H_2O, MnO_2$) are not formed. The products are complex, as $K_2Mn_5O_{11}$. Some less complex manganites are formed in the **Weldon process** for utilizing the manganous chloride obtained in manufacturing chlorine. The liquor is mixed with slaked lime, and air is blown through the mass of calcium and manganous hydroxides which is thus obtained. Black manganites of calcium, such as $CaMnO_3$($= CaO,MnO_2$) and $CaMn_2O_5$($CaO,2MnO_2$) are thus formed:

$$Ca(OH)_2 + 2Mn(OH)_2 + O_2 \rightarrow CaMn_2O_5 + 3H_2O,$$

and when afterwards treated with hydrochloric acid they behave like mixtures of manganese dioxide and calcium oxide. As we have seen (p. 738), the oxides Mn_3O_4 and Mn_2O_3 may be manganites of manganese.

Manganates.—When one of the oxides of manganese is fused with potassium carbonate and potassium nitrate a green mass is obtained. The green aqueous extract deposits potassium manganate K_2MnO_4 in rhombic crystals, which are isomorphous with those of potassium sulphate, and are almost black:

$$K_2CO_3 + MnO_2 + O \rightarrow K_2MnO_4 + CO_2.$$

The acid H_2MnO_4, itself unknown, must be weak, for the potassium salt is easily hydrolyzed. The salt remains unchanged in solution only in presence of free alkali, the hydroxidion of the alkali combin-

ing with and suppressing the hydrion of the water whose combination with the MnO_4'' ion constitutes the hydrolysis. When the concentration of the hydroxidion is reduced by dilution, or, better still, when a weak acid such as carbonic acid or acetic acid is used to neutralize it, the salt is hydrolyzed, according to the partial equation:

$$K_2MnO_4 + 2H_2O \rightarrow 2KOH\,(+\,H_2MnO_4). \qquad (1)$$

The free acid immediately changes so that a part is oxidized to permanganic acid, giving a purple-red color to the solution, and a part is reduced to manganese dioxide, giving a black precipitate. The transformation is similar to that of chloric acid (p. 275). The equation may be made by noting that manganic acid has the composition H_2O, MnO_3 and changes so as to yield H_2O,Mn_2O_7 and MnO_2. Thus each molecule of H_2MnO_4, in forming a molecule of MnO_2, yields one unit of oxygen, while $2(H_2O,MnO_3) + O$ are required to give $H_2O,Mn_2O_7 + H_2O$:

$$3(H_2O, MnO_3) \rightarrow H_2O, Mn_2O_7 + MnO_2 + 2H_2O$$

or

$$(3H_2MnO_4) \rightarrow 2HMnO_4 + MnO_2 + 2H_2O. \qquad (2)$$

In consequence of the presence of potassium hydroxide (equation (1)) the product is potassium permanganate:

$$2KOH + 2HMnO_4 \rightarrow 2KMnO_4 + 2H_2O. \qquad (3)$$

Multiplying equation (1) by 3, omitting the manganic acid, and adding the three partial equations, we have the equation for the action as it really occurs:

$$3K_2MnO_4 + 2H_2O \rightarrow 4KOH + 2KMnO_4 + MnO_2.$$

In terms of the ions the equation is simpler:

$$3MnO_4'' + 2H^{\bullet} \rightarrow 2OH' + 2MnO_4' + MnO_2.$$

The alkaline solution of potassium manganate interacts readily with oxidizable substances. Thus oxalic acid is converted into carbonic acid, and alcohol into acetic acid. The details of the change depend upon the amount of free alkali present and the nature of the product of oxidation. Lower oxides of manganese such as MnO_2 are usually precipitated.

Permanganates. — **Potassium permanganate** $KMnO_4$ is made by hydrolysis of the manganate as shown above, and is obtained, in purple

crystals with a greenish luster, by evaporation of the solution. The crystals are rhombic prisms, isomorphous with potassium perchlorate. To avoid the loss of manganese thrown down as dioxide, the action is carried out commercially by passing ozone through the solution of the manganate:

$$2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + O_2 + 2KOH.$$

Sodium permanganate is made in a similar manner. It is not obtainable in solid form, but its solution is known as "Condy's disinfecting fluid." This liquid owes its properties to the oxidizing power of the salt. **Permanganic acid** is a very active acid, that is, it is highly ionized in aqueous solution. A solid hydrate of the acid may be secured in reddish-brown crystals by adding sulphuric acid to a solution of barium permanganate and allowing the filtrate to evaporate:

$$Ba(MnO_4)_2 + H_2SO_4 + xH_2O \rightleftarrows BaSO_4\downarrow + 2HMnO_4,xH_2O.$$

This hydrate decomposes, on being warmed to 32°, and yields oxygen and manganese dioxide. When a very little dry, powdered potassium permanganate is moistened with concentrated sulphuric acid, brownish-green, oily drops of **permanganic anhydride** (manganese heptoxide) Mn_2O_7 are formed. This compound is volatile, giving a violet vapor, and is apt to decompose explosively into oxygen and manganese dioxide. Its oxidizing power is such that combustibles like paper, ether, and illuminating-gas are set on fire by contact with it.

Potassium permanganate is much used for **oxidations**. The actions are different according as the substance is employed (1) in alkaline, (2) in acid, or (3) in neutral solution.

1. When an alkali, such as potassium hydroxide, is added, the action by which the permanganate is formed is reversed, and the solution becomes green from the production of the manganate:

$$4KMnO_4 + 4KOH \rightarrow 4K_2MnO_4 + 2H_2O + O_2,$$

or

$$4MnO_4' + 4OH' \rightarrow 4MnO_4'' + 2H_2O + O_2.$$

When a substance capable of being oxidized is present, the reduction proceeds further and manganese dioxide is precipitated. Schematically: $Mn_2O_7 \rightarrow 2MnO_2 + 3O$, so that two molecules of the permanganate, in alkaline solution, can furnish three chemical units of oxygen to the oxidizable body.

2. With an acid, the amount of oxygen available is greater, for the manganous salt of the acid is formed:

$$Mn_2O_7 \rightarrow 2MnO + 5O.$$

Thus, when sulphuric acid is added to potassium permanganate solution, and sulphur dioxide is led through the mixture, we have:

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O(+5O) \quad (1)$$
$$(5O) + 5H_2SO_3 \rightarrow 5H_2SO_4 \quad (2)$$
$$2KMnO_4 + 3H_2SO_4 + 5H_2SO_3 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5H_2SO_4$$

In this case, since sulphuric acid is a product, the preliminary addition of the acid was superfluous. In other cases, the partial equation (1), showing the available 5O, remains the same, while the other partial equation varies with the substance being oxidized. Thus, with hydrogen sulphide as reducing agent, we have:

$$(O) + H_2S \rightarrow H_2O + S \quad \times 5 \quad (2')$$

and with ferrous sulphate, we get ferric sulphate:

$$2FeSO_4 + H_2SO_4(+O) \rightarrow Fe_2(SO_4)_3 + H_2O \quad \times 5 \quad (2'')$$

As before (2′) and (2″) must be multiplied throughout by five, before summation is made. Since the permanganate is deep-purple in color, while the manganous salt is almost colorless, this sort of action can be used without an indicator for quantitative experiments. The standard solution of the permanganate is added from a burette until the purple color ceases to disappear; and the amount used enables us to calculate the quantity of ferrous salt, oxalic acid, nitrous acid, or other oxidizable substance, which was present. The last named substance is oxidized to nitric acid.

3. When dry potassium permanganate is heated, it decomposes as follows:

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2.$$

The neutral solution resembles that of potassium dichromate in oxidizing substances which are reducing agents, but is more active. Thus when the powdered salt is moistened with glycerine, the mass presently bursts into flame. The fingers are stained brown, receiving a deposit of manganese dioxide, in consequence of the reducing power of the unstable organic substances in the skin. The destruction of minute organisms by Condy's fluid results from a similar action.

Analytical Reactions of Manganese Compounds. — The ions commonly encountered are dimanganion $Mn^{\cdot\cdot}$, which is very pale-pink in color, permangananion MnO_4', which is purple, and manganananion MnO_4'', which is green.

The manganous compounds give with ammonium sulphide the flesh-colored, hydrated sulphide which is soluble in acids. Bases give the white hydroxide, which darkens by oxidation, and is soluble in salts of ammonium. The black, hydrated dioxide is precipitated by hypochlorites.

All compounds of manganese confer upon the borax bead an amethyst color which, in the reducing flame, disappears. A bead of sodium carbonate and niter becomes green on account of the formation of the manganate.

Exercises. — 1. Consider the valence of manganese in the oxides Mn_3O_4 and Mn_2O_3, on the theory that they are manganites.

2. What do we mean by saying that (*a*) chromous chloride is stable (p. 119), but easily oxidized by the air, (*b*) permanganic acid is an active acid, (*c*) permanganic acid is an active oxidizing agent in presence of an acid?

3. Formulate the oxidations of oxalic acid and of nitrous acid by potassium permanganate in acid solution.

CHAPTER XLIV

IRON, COBALT, NICKEL

THE elements iron (Fe, at. wt. 55.9), cobalt (Co, at. wt. 59), and nickel (Ni, at. wt. 58.7) are not corresponding members of successive periods, like the families hitherto considered. They are neighboring members of the first long period, lying between its first and second octaves (p. 408), and form a transition group between the adjoining elements within those octaves. Thus, iron forms ferrates $M_2^IFe^{VI}O_4$ and ferric salts $Fe^{III}Cl_3$, as well as ferrous salts $Fe^{II}Cl_2$. These resemble the chromates and manganates, the chromic and manganic salts, and the chromous and manganous salts, respectively. Cobalt forms cobaltic and cobaltous salts, like $Co_2^{III}(SO_4)_3$ and $Co^{II}Cl_2$. Nickel enters only into nickelous salts, like $NiCl_2$, and thus links iron and cobalt with copper and zinc which are both bivalent elements. The free metals of this family are magnetic, iron showing this property strongly and cobalt very distinctly.

IRON.

Chemical Relations of the Element. — The oxides and hydroxides FeO and $Fe(OH)_2$, Fe_2O_3 and $Fe(OH)_3$ are basic, the former more strongly so than the latter. The ferrous salts, derived from $Fe(OH)_2$, resemble those of the magnesium group and those of $Cr^{\cdot\cdot}$ and $Mn^{\cdot\cdot}$ and are little hydrolyzed. The ferric salts, derived from $Fe(OH)_3$, resemble those of $Cr^{\cdot\cdot\cdot}$ and $Al^{\cdot\cdot\cdot}$ and are hydrolyzed to a considerable extent. Ferric hydroxide is even less acidic, however, than is chromic hydroxide. Iron gives also a few ferrates K_2FeO_4, $CaFeO_4$, etc., derived from an acid H_2FeO_4 which, like manganic acid H_2MnO_4 (p. 742), is too unstable to be isolated. Complex anions containing this element, such as the anion of $K_4.Fe(CN)_6$, are familiar, but complex cations containing ammonia are unknown.

The ferrous salts differ from most of the manganous salts and resemble the chromous and stannous salts in being easily (although not quite so easily) oxidized by the air. They pass into the ferric condition.

Occurrence. — Free iron is found in minute particles in some basalts, and many meteorites are composed of it. Meteoric iron can be distinguished from specimens of terrestrial origin by the fact that it contains 3–8 per cent of nickel. The chief ores of iron are the oxides, hæmatite Fe_2O_3 and magnetite Fe_3O_4, and the carbonate $FeCO_3$, siderite. The first is reddish and columnar in structure; but black, shining, rhombohedral crystals, known as specularite, are also found. Hydrated forms, like brown iron ore $2Fe_2O_3$, $3H_2O$, are also common. Siderite is pale-brown in color and rhombohedral, isomorphous with calcite. When mixed with clay it forms iron-stone and, with 20–25 per cent of coal in addition, black-band. Pyrite FeS_2 consists of golden-yellow, shining cubes or pentagonal dodecahedra. It is used, on account of its sulphur, in the manufacture of sulphuric acid, but, from the oxidized residue, iron of sufficient purity is obtained with difficulty. Compounds of iron are contained in chlorophyl and in the blood (hæmoglobin), and doubtless play an important part in connection with the vital functions of these substances. By interaction with organic compounds of iron present in the tissues, ammonium sulphide blackens the skin, ferrous sulphide being formed.

Metallurgy. — The ores of iron are usually first roasted in order to decompose carbonates and oxidize sulphides. They are then reduced with coke. Ores containing lime or magnesia are mixed with an acid flux, such as sand or clay-slate, in order that a fusible slag may be formed. Conversely, ores containing silica and clay are mixed with limestone. With proper adjustment of the ingredients the process can be carried on *continuously* in a blast furnace (Fig. 105). The solid materials thrown in at the top are converted, as they slowly descend, completely into gases which escape and liquids (iron and slag) which are tapped off at the bottom. Heated air is blown in at the bottom through

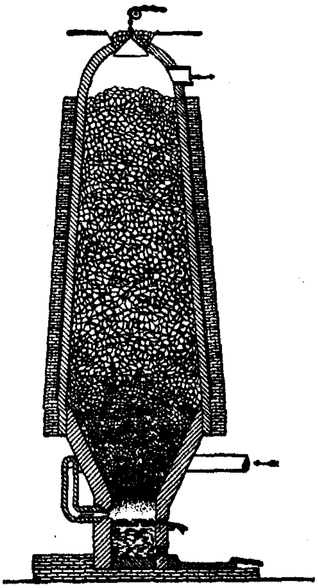


FIG. 105.

tuyères, and the top is closed by a bell which descends for a moment when an addition is made to the charge. The gases, which contain much carbon monoxide, are led off and used to heat the blast or to drive gas-engines.

The main action takes place between the carbon monoxide, present in consequence of the excess of carbon, and the oxide of iron:

$$Fe_3O_4 + 4CO \rightleftarrows 3Fe + 4CO_2.$$

Since the action is a reversible one, a large excess of carbon monoxide is required. Different smelters use different proportions, the ratio of the amount actually used to that supplied varying from 1 : 2 to 1 : 15. The actual ratio by volume of carbon dioxide to carbon monoxide required for equilibrium with the two solids is, 61 : 39 at 650°, and 7 : 93 at 800°.

In the upper part of the furnace, the heat (400°) loosens the texture of the ore. Further down, the temperature is higher (500–900°), and the carbon monoxide reduces the oxide of iron to particles of soft iron. A temperature high enough to melt pure iron is barely reached anywhere in the furnace, but, a little lower down, by union with carbon, the more fusible cast iron (1200°) is formed and falls in drops to the bottom. It is in this region also that the slag is produced. If the flux had begun sooner to interact with the unreduced ore, iron would have been lost by the formation of the silicate. The iron collects below the slag, and the latter flows continuously from a small hole. The former is tapped off at intervals of six hours or so from a lower opening.

Cast Iron and Wrought Iron. — Pure iron is not manufactured, and indeed would be too soft for most purposes. Piano-wire, however, is about 99.7 per cent pure. The product obtained from the blast furnace contains about 90 per cent of iron along with 3–4.5 per cent of carbon, often nearly as much silicon, varying proportions of manganese, and some phosphorus and sulphur. The last four ingredients are liberated from combination with oxygen by the carbon in the hottest part of the furnace and combine or alloy themselves with the iron. Cast iron does not soften before melting, as does the purer wrought iron, but melts sharply at 1150–1250° according to the amount of foreign material it contains. When *suddenly* cooled it gives **white cast iron** which is very brittle and looks homogeneous to the eye, all the carbon being present in the form of carbide of iron Fe_3C in solid solution in the

metal. By slower cooling, time is permitted for the separation of part of the carbon as graphite and for other changes (see below), and **gray cast iron** results. **Spiegel iron** is cast iron made from ores containing 5–20 per cent of manganese and the usual proportion of carbon. **Ferro-manganese** contains 20–80 per cent of the same element.

Wrought iron is made by heating the broken "pigs" of cast iron upon a layer of material containing oxide of iron and hammer-slag (basic silicate of iron) spread on the bed of a reverberatory furnace. The carbon, silicon, and phosphorus combine with the oxygen of the oxide, and the last two pass into the slag. The sulphur is found in the slag as ferrous sulphide. On account of the effervescence due to the escape of carbon monoxide, the process is called "pig-boiling." The iron is stirred with iron rods ("puddled") and stiffens as it becomes purer, until finally it can be withdrawn in balls ("blooms") and freed from slag under the steam-hammer. It now softens sufficiently for welding below 1000° and melts at 1600° or higher, according to its purity. If it still contains more than a trace of combined phosphorus it is brittle when cold ("cold short"). A little surviving sulphide of iron makes it brittle when hot ("red-short") and unsuitable for forging. Wrought iron should contain only 0.1–0.2 per cent of carbon. The above operations are now largely performed by machinery.

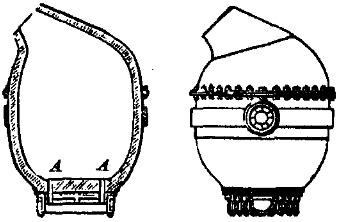


FIG. 106.

Steel. — This is a variety of iron almost free from phosphorus, sulphur, and silicon, and containing usually not more than 1.5 per cent of carbon. "Mild steel" contains 0.2–0.5 per cent of carbon. Steel combines the properties of wrought and of cast iron, being hard and elastic, and at the same time available for forging and welding when the proportion of carbon is not too high.

Steel is made largely by the **Bessemer process**. The molten cast iron is poured into a converter (Fig. 106) and a blast of air (*A*) is blown through it. The oxidation of the manganese, carbon, silicon, and perhaps a little of the iron gives out sufficient heat to raise the temperature of the mass above the melting-point of wrought iron. The required proportion of carbon is then introduced by adding pure

cast iron, spiegel iron, or charcoal, and the contents, first the slag, and then the molten steel, are finally poured into molds by turning the converter. When the cast iron contains much phosphorus, the oxide of this element is reduced again by the iron as fast as it is formed by the blast. In such cases a basic lining containing lime and magnesia takes the place of the sand and clay lining of the ordinary Bessemer converter, and a slag containing a basic phosphate of calcium is produced. This modification constitutes what is known as the Thomas-Gilchrist process. The slag ("Thomas-slag") when pulverized forms a valuable fertilizer (*cf.* p. 605).

In the **Siemens-Martin**, or **open hearth** process, the cast iron is melted in a saucer-shaped depression lined with sand, and scraps of iron plate (for dilution) and hæmatite, or some other oxide ore, are then added in proper proportions. The materials are heated with gas fuel for 8–10 hours until a sample shows, under the hammer, that the process is complete. The product is then drawn off through a hole and cast in molds.

Properties of Steel. — When steel is heated to redness and cooled slowly, it is comparatively soft. Sudden chilling, however, renders it harder than glass. By subsequent, cautious heating the hardness may be reduced to any required extent, and this treatment is called "tempering." The sufficiency of the heating is judged roughly by the interference colors caused by the thin film of oxide which forms on the surface. Thus a pale-yellow color (430–450° F) serves for tempering razors, a decided yellow (470°) for pen-knives, a brown (490–510°) for shears, a purple (520°) for table-knives, a blue (530–570°) for watch-springs and sword-blades, and a black-blue (610°) for saws. Except in the case of watch-springs, these films are afterwards removed by the grinding.

To understand this behavior it must be noted that there are three states of solid iron resembling the rhombic and monoclinic states of sulphur (*cf.* p. 368). The form stable below 765° is known as α-ferrite (wrought iron). It is magnetic and can hold little carbide of iron in solid solution. Above 765° this changes into β-ferrite which, likewise, holds little of the carbide in solution, but is not magnetic. At 890° this changes into γ-ferrite, a non-magnetic form in which the carbide is soluble. When allowed to cool, iron assumes these forms in the reverse order. If, now, a fluid solution of carbon in iron, suitable for steel, is *suddenly chilled*, a great part of the cold mass is a supercooled solid

solution of carbide of iron in γ-ferrite. This material is called martensite and is very hard and brittle. It is less stable at ordinary temperatures than is α-ferrite, but, as is the case with yellow phosphorus (p. 359) and amorphous sulphur (p. 370), the low temperature having once been reached, transformation into the more stable form is thereafter exceedingly slow. The material is hard steel.

When the molten steel (solution of carbon in iron) is *allowed to cool* so *slowly* that equilibrium can be reached at every step, a complicated series of changes ensues. First the mass solidifies (at or before 1130°) to a mixture of martensite (γ-ferrite with carbide in solid solution up to 2 per cent) and graphite.* As the temperature now falls very slowly, more graphite separates until, at 1000°, 1.8 per cent remains in solution. From this point the dissolved carbide of iron (cementite Fe_3C containing 6.6 per cent of carbon) is separated. At 670° pure α-ferrite also begins to appear. The final result is a mechanical mixture of α-ferrite (wrought iron), carbide of iron, and, if the original amount of carbon was sufficiently large, graphite. These components may be recognized by making a microscopic study of a polished surface, and their formation may be followed by chilling the specimen at any desired stage. The soft iron which predominates in the product of slow cooling makes the whole soft. Heating to a high temperature and sudden chilling gives the homogeneous solid solution of the carbide in γ-ferrite once more and restores the qualities characteristic of steel. Moderated reheating (tempering) of the chilled mass results in more or less partial accomplishment of the changes proper to slow cooling, and consequently in a more or less close approach to the condition which results from this.

The difference between the effect of rapid and slow cooling of cast iron (p. 748) can now be made clear. Rapid cooling leads to the omission of the intervening steps enumerated above and, if something like 5 or 6 per cent of carbon is present, the material turns almost completely into the carbide (cementite). This is white cast iron. With slower cooling, much graphite separates, and the product, gray cast iron, contains much less of the carbide and much more free iron.

The various changes which occur in cooling steel are retarded by the presence of foreign substances, just as, with sulphur (p. 370), foreign substances delay the change from S_μ to S_λ and permit the supercooling of the former and its appearance in the form of amorphous

* When molten cast iron, containing 3–4.5 per cent of carbon, is cooled in this fashion, the amount of graphite may be considerable.

sulphur. Manganese, nickel, and other metals, in particular, greatly reduce the facility with which γ-ferrite passes into β- and α-ferrite at 890° and 765°. Thus iron with 12 per cent of manganese, when chilled from a high temperature, contains only supercooled γ-ferrite and is non-magnetic. It has to be kept for hours (instead of a few minutes) at a temperature below 765°, say 500–600°, before it goes over into α-ferrite. Manganese is thus a valuable constituent of steel because, by favoring the survival of the γ-ferrite in which alone the carbon is soluble, it permits the manufacture of a homogeneous steel containing an unusually large proportion of dissolved carbon, and allows slower cooling without loss of temper.

Pure Iron. — The pure metal may be made by reducing the purified oxalate in a stream of hydrogen or by Goldschmidt's method (p. 540).

Chemical Properties. — When exposed to moist air, iron receives a loosely adherent coating of rust ($2Fe_2O_3, Fe(OH)_3$). There is still uncertainty as to how the product is formed. It may result from displacement of the hydrogen of carbonic acid, the oxygen assisting (*cf.* p. 624), and subsequent hydrolysis of the carbonate and oxidation of the ferrous hydroxide. The fact that alkalies prevent rusting favors this view, for they should diminish the amount of hydrion. According to another theory, water and iron are simultaneously oxidized:

$$Fe + O_2 + H_2O \rightarrow FeO + H_2O_2$$

and the hydrogen peroxide immediately combines with the ferrous oxide:

$$2FeO + H_2O_2 \rightarrow Fe_2O_2(OH)_2. \qquad (2)$$

The presence of the peroxide cannot be demonstrated in this case, perhaps because it is used up very rapidly. In the rusting of zinc, however, it is always found (*cf.* also p. 636).

Iron burns in oxygen and interacts with superheated steam, giving Fe_3O_4. A superficial layer of this oxide adheres firmly and protects the iron from the action of the air (Barff's process for prevention of rusting).

Iron displaces hydrogen easily from dilute acids. Steel and cast iron, which contain iron, its carbide, and graphite, give with cold dilute acids almost pure hydrogen, and the carbide and graphite remain unattacked. More concentrated acids, however, particularly when warm,

give off, along with hydrogen, hydrocarbons formed by interaction with the carbide (p. 543). The odor of the gas is due to compounds of sulphur and phosphorus. With dilute nitric acid, iron gives ferrous nitrate and ammonium nitrate (*cf.* tin, p. 694) and with the concentrated nitric acid ferric nitrate and oxides of nitrogen. It has little action upon alkalies.

After being dipped in very concentrated nitric acid, iron becomes passive (*cf.* chromium, p. 723), and no longer displaces hydrogen and other elements lying below it in the electromotive series. A sharp blow, however, produces a change which spreads over the surface from the point struck, and the metal becomes active once more.

Ferrous Compounds. — **Ferrous chloride** is obtained as a pale-green hydrate $FeCl_2, 4H_2O$ by interaction of hydrochloric acid with the metal or the carbonate. The anhydrous salt sublimes in colorless crystals when hydrogen chloride is led over the heated metal. At a high temperature the vapor of ferrous chloride has a density corresponding to the simple formula $FeCl_2$, but at lower temperatures there is much association (p. 242) and the formula approaches Fe_2Cl_4. In solution the salt is oxidized by the air to a basic ferric chloride:

$$4Fe^{\cdot\cdot} + O_2 + 2H_2O \rightarrow 4Fe^{\cdot\cdot\cdot} + 4OH.'$$

In presence of excess of the acid, normal ferric chloride is formed. With nitric acid, ferric chloride and nitric oxide are produced (p. 442).

Ferrous hydroxide $Fe(OH)_2$ is thrown down as a white precipitate, but rapidly becomes dirty-green and finally brown, by oxidation. It dissolves in solutions of salts of ammonium, being, like magnesium hydroxide (p. 644), sufficiently soluble in water to require an appreciable concentration of OH′ for its precipitation. The ammonium salts convert this into molecular ammonium hydroxide. **Ferrous oxide** FeO is black, and is formed by heating ferrous oxalate in absence of air. It may be made also by cautious reduction of ferric oxide by hydrogen (at about 300°), but is easily reduced further to the metal.

Ferrous carbonate is found in nature, and may be made in slightly hydrolyzed form by precipitation. The precipitate is white but rapidly darkens and finally becomes brown, the ferrous hydroxide produced by hydrolysis being oxidized to the ferric condition. The salt interacts with water containing carbonic acid after the manner of calcium carbonate (p. 482), and hence is found in solution in natural (chalybeate) waters.

Ferrous sulphide may be formed as a black, metallic-looking mass by heating together the free elements. It is produced by precipitation with ammonium sulphide, but not with hydrogen sulphide. It interacts readily with dilute acids. The precipitated form is slowly oxidized to ferrous sulphate by the air.

Ferrous sulphate is obtained by allowing pyrites to oxidize in the air and leaching the residue:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4.$$

The liquor is treated with scrap iron and the neutral solution evaporated until a hydrate $FeSO_4, 7H_2O$, green vitriol, or "copperas," is deposited. This substance forms green crystals belonging to the monosymmetric system, but gives also mixed crystals in which it is isomorphous with the rhombic vitriols (*cf.* Magnesium and Zinc sulphates, p. 649). The crystals are efflorescent, and become also brown from oxidation to a basic ferric sulphate:

$$4FeSO_4 + O_2 + 2H_2O \rightarrow 4Fe(OH)SO_4.$$

With excess of sulphuric acid and air, or an oxidizing agent, such as nitric acid, ferric sulphate is formed. The anhydrous salt forms a molecular compound with nitric oxide, and the solution becomes brown when this gas is led through it, an unstable complex ion, perhaps $FeNO^{\cdot\cdot}$, being produced (*cf.* p. 443). The double salts of the form $(NH_4)_2SO_4, FeSO_4, 6H_2O$ (Mohr's salt) are not efflorescent, and in solid form are less readily oxidized than is ferrous sulphate. The ferrous sulphate is used in dyeing and in making **ink**. The extract of nut-galls contains tannic acid, $HC_{14}H_9O_9$, which, with ferrous sulphate, gives ferrous tannate. This salt is oxidized by the air to the ferric condition, and the ferric compound is a fine, black precipitate which can be suspended in a solution of gum-arabic. The resulting material is ink. The black streaks seen below nail-heads in oak and other woods are due to the formation of ferrous carbonate and its interaction with the tannic acid in the wood.

Ferric Compounds. — By leading chlorine into a solution of ferrous chloride, and evaporating until the proper proportion of water alone remains, a yellow, deliquescent hydrate of **ferric chloride**, $FeCl_3, 6H_2O$ is obtained. When this is heated still further, hydrolysis takes place and the oxide remains. When chlorine is passed over heated iron, the anhydrous salt sublimes in dark scales, which are red by

transmitted light. At a high temperature the formula of the vapor is $FeCl_3$, but at lower temperatures, in consequence of association, the density increases and the formula approaches Fe_2Cl_6. In solution, the salt, like other ferric salts, can be reduced to the ferrous condition by boiling with iron:

$$2Fe^{\cdot\cdot\cdot} + Fe \rightarrow 3Fe^{\cdot\cdot}.$$

The same reduction is effected by hydrogen sulphide and by stannous chloride (*cf.* Mercuric chloride, p. 655):

$$2Fe^{\cdot\cdot\cdot} + S'' \rightarrow 2Fe^{\cdot\cdot} + S\downarrow.$$
$$2Fe^{\cdot\cdot\cdot} + Sn^{\cdot\cdot} \rightarrow 2Fe^{\cdot\cdot} + Sn^{\cdot\cdot\cdot\cdot}.$$

The last action shows that ferrous salts are less active reducing agents than are the stannous salts. The ferric ion is almost colorless, the yellow-brown color of solutions of ferric salts being due to the presence of ferric hydroxide produced by hydrolysis. The color deepens when the solution is heated, and fades again very slowly, by reversal of the action, when the cold solution is allowed to stand. On the other hand, the hydrolysis may be reversed and the color may be almost destroyed, particularly in the case of the nitrate, when excess of the acid is added to the solution:

$$Fe(NO_3)_3 + 3H_2O \leftrightarrows Fe(OH)_3 + 3HNO_3.$$

Ferric iodide is reduced by the hydriodic acid produced by its own hydrolysis, and hence ferrous iodide does not unite with iodine to form this compound. The case is similar to that of cupric iodide (p. 621).

Ferric hydroxide, $Fe(OH)_3$, appears as a brown precipitate when a base is added to a ferric salt. It does not interact with excess of the alkali. In this form the substance is a hydrogele (p. 523) and dries to the oxide without giving definite intermediate hydrated oxides. The hydrates, $Fe_4O_3(OH)_6$ (brown iron ore) and $Fe_2O(OH)_4$ (bog iron ore), however, are found in nature. The hydroxide passes easily into colloidal solution in a solution of ferric chloride, and by subsequent dialysis through a piece of parchment (*cf.* p. 523) the salt can be separated, and a pure aqueous solution of the hydroxide obtained. This solution is red in color, shows no depression in the freezing-point, and is not an electrolyte. It deposits the hydroxide as a brown precipitate when ionogens are added to the solution.

Ferric oxide, Fe_2O_3, is sold as "rouge" and "Venetian red." It is made from the ferrous sulphate obtained in cleaning iron ware which

is to be tinned or galvanized, and in other ways in the arts. The salt is allowed to oxidize, and the ferric hydroxide, thrown down by the addition of lime, is calcined. A purer form is produced by dry distillation of the basic ferric sulphate, an operation which used to be undertaken on a large scale for making Nordhausen sulphuric acid (p. 388). This oxide is not distinctly acidic, but by fusion with more basic oxides, compounds like franklinite $Zn(FeO_2)_2$ may be formed. It is reduced by hydrogen, at about 300° to ferrous oxide (which catches fire spontaneously in the air) and at 700–800° to metallic iron.

Magnetic oxide of iron Fe_3O_4 or lodestone is found in nature, and is formed by the action of air (hammer-scale), steam, or carbon dioxide on iron. It forms octahedral crystals like the spinelles (p. 686), and is assumed to be $Fe(FeO_2)_2$.

Ferric sulphide may be made by fusing together the free elements but is not obtained by precipitation. Soluble sulphides first reduce the ferric salt to the ferrous conditions, liberating sulphur,

$$Fe_2(SO_4)_3 + (NH_4)_2S \rightarrow 2FeSO_4 + (NH_4)_2SO_4 + S,$$

and then give ferrous sulphide (p. 376).

Ferric sulphate is formed by oxidation of ferrous sulphate, and is obtained as a white mass by evaporation. It gives alums, such as $(NH_4)_2SO_4, Fe_2(SO_4)_3, 24H_2O$, which are almost colorless when pure, but usually have a pale reddish-violet tinge.

Pyrite.—The mineral pyrite FeS_2 (Fools' gold) is the sulphide of iron which is most stable in the air. It is found in nature in the form of glittering, golden-yellow cubes, octahedrons, and pentagonal dodecahedrons. It is not attacked by dilute acids, but concentrated hydrochloric acid slowly converts it into ferrous chloride and sulphur. It is reduced by hydrogen to ferrous sulphide.

Cyanides.— When potassium cyanide is added to solutions of ferrous or ferric salts, yellowish precipitates are produced, but the simple cyanides cannot be obtained in pure form. These precipitates interact with excess of the cyanide giving soluble complex cyanides of the forms $4KCN, Fe(CN)_2$ and $3KCN, Fe(CN)_3$ respectively. These are called ferro- and ferricyanide of potassium, respectively.

Ferrocyanide of potassium, "yellow prussiate of potash," is made by heating nitrogenous animal refuse, such as blood, with iron filings

and potassium carbonate. The resulting mass contains potassium cyanide and ferrous sulphide, and when it is treated with warm water these interact and produce the ferrocyanide:

$$2KCN + FeS \rightarrow Fe(CN)_2 + K_2S,$$
$$4KCN + Fe(CN)_2 \rightarrow K_4.Fe(CN)_6.$$

The salt is made also from the cyanogen contained in crude illuminating-gas. It forms large, yellow, monosymmetric tables with three molecules of water of hydration. The solution contains almost exclusively the ions $K^{\cdot}$ and $Fe(CN)_6''''$, and gives none of the reactions of the ferrous ion $Fe^{\cdot\cdot}$. The corresponding acid $H_4Fe(CN)_6$ may be obtained as white crystalline scales by addition of an acid and of ether (in which the substance is less soluble than in water) to the salt. The acid is a fairly active one but is unstable and decomposes in a complex manner. Other ferrocyanides may be made by precipitation. That of copper $Cu_2Fe(CN)_6$ is brown, and ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$ has a brilliant blue color ("Prussian blue"). The ferrous compound $Fe_2Fe(CN)_6$, or perhaps $K_2FeFe(CN)_6$, is white but quickly becomes blue by oxidation. The ferrocyanides are not poisonous.

Ferricyanide of potassium. This salt is easily made from the ferrocyanide by oxidation:

$$2K_4Fe(CN)_6 + Cl_2 \rightarrow 2KCl + 2K_3Fe(CN)_6,$$

or

$$2Fe(CN)_6'''' + Cl_2 \rightarrow 2Fe(CN)_6''' + 2Cl'.$$

It forms red monosymmetric prisms. The free acid $H_3Fe(CN)_6$ is unstable. Other salts may be prepared by precipitation. Ferrous ferricyanide $Fe_3[Fe(CN)_6]_2$ is deep-blue in color ("Turnbull's blue"). With ferric salts only a brown solution is obtained.

Ferric thiocyanate $Fe(CNS)_3$ is formed by interaction of soluble thiocyanates with ferric salts (*cf.* p. 250). It is deep-red in color and gives a blood-red solution in water. Since both the ions are colorless, the solution must contain chiefly the molecular salt. Its formation furnishes a very delicate test for traces of ferric salts.

Iron Carbonyls. — When carbon monoxide is led over finely divided iron at 40–80°, or under eight atmospheres pressure at the ordinary temperature, volatile compounds of the composition $Fe(CO)_4$, the tetracarbonyl, and $Fe(CO)_5$, the pentacarbonyl, are formed. When

the gaseous mixture is heated more strongly, the compounds decompose again, and iron is deposited. Illuminating-gas burners frequently receive a deposit of iron from this cause.

Ferrates. — A red solution of potassium ferrate, K_2FeO_4, is obtained by passing chlorine through caustic potash in which ferric hydroxide is suspended. The salt crystallizes in red, rhombic prisms, isomorphous with the sulphate and chromate of potassium. It alters quickly in solution, in consequence of hydrolysis and subsequent decomposition of the ferric acid, depositing ferric hydroxide and giving off oxygen. Barium, strontium, and calcium salts are formed as red precipitates by double decomposition.

Analytical Reactions of Compounds of Iron. — There are two ionic forms of iron, diferrion $Fe^{\bullet\bullet}$, which is very pale-green, and triferrion $Fe^{\bullet\bullet\bullet}$, which is almost colorless. The yellow color of ferric salts is due to hydrolysis. Ammonium sulphide forms, with both, black ferrous sulphide which is soluble in dilute acids. The hydroxides are white and brown respectively, and ferrous carbonate is white. With ferric salts, soluble carbonates yield the hydroxide. With ferrocyanide of potassium, ferrous salts give a white, and ferric salts a blue, precipitate. With ferricyanide of potassium the former give a deep-blue precipitate, and the latter a brown solution. Ferric thiocyanate is deep-red. From ferric solutions barium carbonate throws down ferric hydroxide. When sodium acetate is added in excess to a ferric salt, a red, little ionized, but much hydrolyzed, acetate is formed. When the solution is boiled the hydrolysis is increased, and an insoluble, basic ferric acetate is thrown down. With borax, iron compounds give a bead which is green in the reducing flame, and colorless or, with much iron, yellow or even brown when oxidized.

COBALT.

The Chemical Relations of the Element. — Cobalt forms cobaltous and cobaltic oxides and hydroxides CoO and $Co(OH)_2$, Co_2O_3 and $Co(OH)_3$, respectively, which are all basic, the former more so than the latter. The cobaltous salts are little hydrolyzed, but the cobaltic salts are completely decomposed by water. The latter also liberate readily one-third of the negative radical, after the manner of manganic salts, becoming cobaltous. Complex cations and anions containing cobalt are very numerous and very stable.

Occurrence. — Cobalt is found along with nickel in smaltite $CoAs_2$ and cobaltite CoAsS. The pure metal may be made by Goldschmidt's process, or by reducing the oxalate, or an oxide, with hydrogen.

Physical and Chemical Properties. — The metal is silver-white, with a faint suggestion of pink. It is less tough than iron, and has no commercial applications. It displaces hydrogen slowly from dilute acids, but interacts readily with nitric acid.

Cobaltous Compounds. — The **chloride** may be made by treating the oxide with hydrochloric acid. It forms red prisms of $CoCl_2$, $6H_2O$, and when partially or completely dehydrated becomes deep-blue. Writing made with a diluted solution upon paper is almost invisible, but becomes blue when warmed and afterwards takes up moisture from the air, and is once more invisible ("sympathetic ink"). Most cobaltous compounds are red when hydrated or in solution ($Co^{\bullet\bullet}$) and blue when dehydrated. The blue color assumed by a strong solution of cobaltous chloride, when it is warmed, or when hydrochloric acid is added to it, is explained by some chemists as being due to repression of the ionization of the salt, and by others as being due to the formation of the complex anion of the salt $Co^{\bullet\bullet}.CoCl_4''$. By addition of sodium hydroxide to a cobaltous salt, a blue basic salt is precipitated. When the mixture is boiled, the red **hydroxide**, $Co(OH)_2$ is formed. This becomes brown through oxidation by the air. It interacts with ammonium hydroxide, giving a soluble ammonio-cobaltous hydroxide (*cf.* p. 661), which is quickly oxidized by the air to an ammonio-cobaltic compound (see below). It dissolves also in salts of ammonium as magnesium hydroxide does (p. 644). When dehydrated it leaves the black **cobaltous oxide**. **Cobaltous sulphate**, $CoSO_4$, $7H_2O$, isomorphous with magnesium sulphate, and the **nitrate**, $Co(NO_3)_2$, $6H_2O$, are familiar salts. The black **cobaltous sulphide**, CoS, is precipitated by ammonium sulphide from solutions of all salts, and even by hydrogen sulphide from the acetate, or a solution containing much sodium acetate (*cf.* p. 650). Once it has been formed, it does not interact even with dilute hydrochloric acid, having apparently changed into a less active form. A sort of **cobalt glass**, made by fusing sand, cobalt oxide, and potassium nitrate, forms, when powdered, a blue pigment ("smalt") used in china-painting and by artists.

Cobaltic Compounds. — By addition of a hypochlorite to a solution of a cobaltous salt, **cobaltic hydroxide** $Co(OH)_3$, a black powder, is precipitated. Cautious ignition of the nitrate gives **cobaltic oxide**, Co_2O_3. Stronger ignition gives the commercial oxide, which is a **cobalto-cobaltic oxide** Co_3O_4. Cobaltic oxide dissolves in cold hydrochloric acid, but the solution gives off chlorine when warmed. By placing cobaltous sulphate round the anode of an electrolytic cell, crystals of **cobaltic sulphate**, $Co_2(SO_4)_3$, have been made and cobaltic alums have also been prepared.

Complex Compounds. — Potassium cyanide precipitates from cobaltous salts a brownish-white cyanide which interacts with excess of the reagent, giving a solution of potassium cobaltocyanide $K_4Co(CN)_6$ (*cf.* p. 756). This compound is easily oxidized by chlorine, or even when the solution is boiled in the air, and the colorless potassium cobalticyanide is formed:

$$4K_4Co(CN)_6 + 2H_2O + O_2 \rightarrow 4K_3.Co(CN)_6 + 4KOH.$$

The solution gives none of the reactions of $Co^{\cdot\cdot\cdot}$, and with acids the very stable cobalticyanic acid, $H_3Co(CN)_6$, is liberated.

When acetic acid and potassium nitrite are added to a cobaltous salt the latter is oxidized by the nitrous acid (liberated by the acetic acid) and a white complex salt $K_3.Co(NO_2)_6, nH_2O$ $(= Co(NO_2)_3, 3KNO_2)$, potassium cobaltinitrite, is thrown down.

Cobaltic salts give with ammonia complex compounds which are many and various. The cations often contain negative groups, and are such as $Co(NH_3)_6^{\cdot\cdot\cdot}$, $Co(NH_3)_5Cl^{\cdot\cdot}$ and $Co(NH_3)_5NO_2^{\cdot\cdot}$. Usually the solutions give none of the reactions of cobaltic ions, and often fail likewise to give those of the anion of the original salt.

NICKEL.

The Chemical Relations of the Element. — Nickel forms nickelous and nickelic oxides and hydroxides NiO and $Ni(OH)_2$, Ni_2O_3, and $Ni(OH)_3$, but only the former are basic. The nickelous salts resemble the cobaltous and ferrous salts, but are not oxidizable into corresponding nickelic compounds. Since there are no nickelic salts, there are here no analogues of the cobalticyanides or the cobaltinitrites. The complex nickelous salts, like the complex cobaltous salts, and unlike the complex cobaltic salts, are unstable, and so give some of the reactions of $Ni^{\cdot\cdot}$.

Occurrence. —Nickel occurs free in meteorites and in niccolite NiAs and nickel glance NiAsS. It is now manufactured chiefly from garnierite, a silicate of nickel and magnesium found in New Caledonia.

Properties. — The metal is white, with a faint tinge of yellow, is very hard, and takes a high polish. It is used in making alloys, such as German silver (copper, zinc, nickel, 2 : 1 : 1) and the "nickel" used in coinage (copper, nickel, 3 : 1). Nickel plating on iron is accomplished exactly like silver plating (p. 632). The bath contains an ammoniacal solution of ammonium-nickel sulphate $(NH_4)_2SO_4, NiSO_4, 6H_2O$, and a plate of nickel forms the anode.

The metal rusts very slowly in moist air. It displaces hydrogen with difficulty from dilute acids but interacts with nitric acid.

Compounds of Nickel. — The **chloride** $NiCl_2, 6H_2O$, is made by treating one of the oxides with hydrochloric acid, and is green in color (when anhydrous, brown). The **sulphate**, $NiSO_4, 6H_2O$, which crystallizes in square prismatic forms at 30–40°, is the most familiar salt. The heptahydrate $NiSO_4, 7H_2O$, obtained from cold solutions, is isomorphous with magnesium sulphate. **Nickelous hydroxide**, $Ni(OH)_2$, is formed as an apple-green precipitate, and when heated leaves the green **nickelous oxide**, NiO. It dissolves in ammonium hydroxide, giving a complex nickel-ammonia cation. It is soluble also in salts of ammonium (*cf.* p. 661). By cautious ignition of the nitrate, **nickelic oxide**, Ni_2O_3, is formed as a black powder. The oxides and salts, when heated strongly in oxygen give the oxide Ni_3O_4. The last two oxides liberate chlorine when treated with hydrochloric acid, and give nickelous chloride. **Nickelic hydroxide**, $Ni(OH)_3$, is a black precipitate formed when a hypochlorite is added to any salt of nickel. **Nickelous sulphide** is thrown down by ammonium sulphide, and behaves like cobaltous sulphide (p. 759). It forms a brown colloidal solution when excess of the precipitant is used, and is then deposited very slowly.

With potassium cyanide and a salt of nickel the greenish **nickelous cyanide**, $Ni(CN)_2$, is first precipitated. This dissolves in excess of the reagent, and a complex salt $K_2Ni(CN)_4, H_2O (= 2KCN, Ni(CN)_2)$ may be obtained from the solution. This salt is of different composition from the corresponding compounds of cobalt and iron, and is less stable. Thus, with bleaching powder, it gives $Ni(OH)_3$ as a black precipitate. When the solution is boiled in the air no oxidation to a complex nickelicyanide occurs, and indeed no such salts is known.

This fact enables the chemist to separate cobalt and nickel, for when the mixed cyanides are boiled and then treated with bleaching powder, the cobalticyanide is unaffected. With potassium nitrite and acetic acid no insoluble compound corresponding to that given by cobalt salts is formed by salts of nickel. The only known compound which could be formed, $4KNO_2,Ni(NO_2)_2$, is soluble. This action also is used for the purpose of separation.

When finely divided nickel, made by reducing the oxide or oxalate with hydrogen at a moderate temperature, is exposed to a stream of cold carbon monoxide, **nickel carbonyl** $Ni(CO)_4$ is formed. This is a vapor and is condensable to a colorless liquid (b.-p. 43° and m.-p. −25°). The vapor is poisonous. When heated to 150–180° it is dissociated and nickel is deposited. Cobalt forms no corresponding compound.

Analytical Reactions of Compounds of Cobalt and Nickel. — The cobalt ion $Co^{\cdot\cdot}$ is pink, and the nickelous ion $Ni^{\cdot\cdot}$ green. The reactions used in analysis have been described in the preceding paragraphs. With borax, cobalt compounds give a blue bead, and nickel compounds a bead which is brown in the oxidizing flame and cloudy, from the presence of gray, metallic nickel, when reduced.

Exercises. — 1. What would be the interactions of calcium carbonate when fused with sand and with clay, respectively?

2. Make equations representing (*a*) the oxidation of ferrous chloride by air, (*b*) the hydrolysis of ferrous carbonate and the oxidation of ferrous hydroxide, (*c*) the oxidation of ferrous sulphate with excess of sulphuric acid by hypochlorous acid, (*d*) the formation of ferrous and ferric tannates (p. 754), (*e*) the reduction of ferric chloride by iron, by hydrogen sulphide, and by stannous chloride, respectively, (*f*) the dry distillation of basic ferric sulphate, (*g*) the formation of ferric ferrocyanide and of ferrous ferricyanide, (*h*) the hydrolysis and decomposition of potassium ferrate.

3. Explain the solubility of cobaltous and nickelous hydroxide in salts of ammonium.

4. Construct equations to show the formation (*a*) of the insoluble potassium cobaltinitrite (nitric oxide is given off), (*b*) of nickelic hydroxide from nickelous chloride and sodium hypochlorite.

5. Tabulate in detail the chemical relations of the elements cobalt and nickel, with especial reference to showing the resemblances and differences.

CHAPTER XLV

THE PLATINUM METALS

THE remaining elements of Mendelejeff's eighth group divide themselves into two sets of three each. Just as iron, cobalt, and nickel have similar atomic weights and much the same specific gravity, (7.8–8.8), so ruthenium (Ru, at. wt. 101.7), rhodium (Rh, at. wt. 103), and palladium (Pd, at. wt. 106.5) have specific gravities from 12.26 to 11.5. Similarly osmium (Os, at. wt. 191), iridium (Ir, at. wt. 193), and platinum (Pt, at. wt. 194.8) form a triad with specific gravities from 22.5 to 21.5. Chemically, ruthenium shows the closest resemblance to osmium, and both are allied to iron. Similarly, rhodium and iridium, and palladium and platinum are natural pairs.

The six elements are found alloyed in nuggets and particles which are separated from alluvial sand by washing. Platinum forms 60–84 per cent of the whole. The chief deposits are in the Ural Mountains, smaller amounts being found in California, Australia, Borneo, and elsewhere. The components are separated by a complex series of chemical operations.

Ruthenium and Osmium. — These metals are gray like iron, while the other four are whiter and more like cobalt and nickel. They also resemble iron in being the most infusible members of their respective sets. Both melt considerably above 2000°. They likewise resemble iron in uniting easily with free oxygen, while the other four elements do not. Ruthenium gives RuO_2 and even RuO_4, although the latter oxide is more easily obtained indirectly. Osmium gives OsO_4, "osmic acid," a white crystalline body melting at 40° and boiling at about 100°. The odor and irritating effects of the vapor recall chlorine (Gk., ὀσμή, odor). The substance is not an acid, or even an acid anhydride. The aqueous solution is used in histology, and stains tissues in consequence of its reduction by organic bodies to metallic osmium. It is affected particularly by fat. Osmic acid also hardens the material without distorting it. It will be observed that ruthenium and osmium have a maximum valence of eight.

These elements resemble iron in giving ruthenates and osmates,

like K_2RuO_4 and K_2OsO_4, but no corresponding oxide or acid. Potassium ruthenate resembles potassium manganate and gives, when diluted, an oxide of ruthenium and potassium perruthenate $KRuO_4$. There are also salts corresponding to the oxides Ru_2O_3 and Os_2O_3.

Rhodium and Iridium. — These metals are not attacked by *aqua regia*, while the other four are dissolved, more or less slowly. They are harder than platinum, and iridium is alloyed with this metal for the purpose of increasing its resistance to the action of acids. They resemble cobalt in having no acid-forming properties. Salts corresponding to the oxides Rh_2O_3 and Ir_2O_3 are formed, and iridium gives compounds derived from IrO_2 as well. The most familiar compounds of iridium are the complex chlorides X_3IrCl_6 (= $3XCl,IrCl_3$) and X_2IrCl_6 (= $2XCl,IrCl_4$). The solutions of the latter are red, and the acid, chloroiridic acid H_2IrCl_6, is often found in commercial chloroplatinic acid H_2PtCl_6, and confers upon it a deeper color.

Palladium and Platinum. — Palladium is the only metal of this family which is attacked by nitric acid. Palladium and platinum form *-ous* and *-ic* compounds of the forms PdX_2 and PdX_4 respectively. The oxides PdO and PtO and corresponding hydroxides are basic. When quadrivalent, the metals appear chiefly in complex compounds, like $H_2.PtCl_6$, $H_2.PdCl_6$, in which the metal is in the anion. Platinum gives also platinates derived from the oxide PtO_2, and quadrivalent platinum furnishes no well defined salts in which it constitutes by itself the positive ion.

Palladium. — This metal, named from the planetoid Pallas, is noted chiefly for its great tendency to absorb hydrogen. At 1000° it takes up about 650 times its own volume. The amount absorbed varies continuously with the concentration (pressure) of the hydrogen, although not according to a uniform rule, and the case is therefore regarded as being one of solid solution. When a strip of palladium is made the cathode of an electrolytic cell, over 900 volumes of hydrogen may be occluded. This absorbed hydrogen, in consequence of the catalytic influence of the metal, reacts more rapidly than does the gas, and consequently a strip of hydrogenized palladium will quickly precipitate copper and other metals less electro-positive than hydrogen and will reduce ferric and other reducible salts:

$$CuSO_4 + H_2 \rightarrow H_2SO_4 + Cu, \quad \text{or} \quad Cu^{\cdot\cdot} + H_2 \rightarrow 2H^{\cdot} + Cu.$$
$$2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl, \quad \text{or} \quad 2Fe^{\cdot\cdot\cdot} + H_2 \rightarrow 2Fe^{\cdot\cdot} + 2H^{\cdot}.$$

The palladious salts are such as $PdCl_2$, $PdSO_4$, $Pd(NO_3)_2$. Palladic chloride, formed by treating the metal with *aqua regia*, is contained in the solution in the form of chloropalladic acid H_2PdCl_6 (= $2HCl$, $PdCl_4$) and gives difficultly soluble salts like K_2PdCl_6. When the solution of the acid is boiled, however, chlorine is given off and $PdCl_2$ or H_2PdCl_4 remains in solution.

Platinum. — This metal (dim. of Sp. *plata*, silver) is grayish-white in color, and is very ductile. At a red heat it can be welded. It does not melt in the Bunsen flame but fuses easily in the oxyhydrogen jet. On account of its very small chemical activity it is used in electrical apparatus and for making wire, foil, and crucibles and other vessels for use in laboratories. It unites, however, with carbon, phosphorus, and silicon, becoming brittle, and forms fusible alloys with metals like antimony and lead. Hence care has to be taken not to heat in vessels made of it compounds from which these elements may be liberated. It also interacts with fused alkalies, giving platinates, but the alkali carbonates may be melted in vessels of platinum with impunity. The oxygen acids are without action upon it, but the free chlorine in *aqua regia* converts it into chloroplatinic acid H_2PtCl_6.

The metal condenses oxygen upon its surface and it dissolves hydrogen. The finely divided forms of the metal, such as **platinum sponge** made by igniting ammonium chloroplatinate $(NH_4)_2PtCl_6$, and **platinum black** made by adding zinc to chloroplatinic acid, show this behavior very conspicuously. They cause instant explosion of a mixture of oxygen and hydrogen, in consequenc of the heat developed by the rapid union of that part of the gases which is condensed in the metal. A heated spiral of fine platinum wire will continue to glow if immersed in the mixture of alcohol vapor and oxygen formed by leading oxygen through liquid alcohol. The heat is developed by the interaction which takes place between the substances with great speed at the surface of the platinum. Platinum sponge is the active constituent of the contact-mass used in making sulphur trioxide (p. 380).

Platinum is the only otherwise suitable substance which has the same coefficient of expansion as glass, and it is consequently fused into incandescent bulbs and furnishes the electrical connection with the filament in the interior. Large amounts are also consumed in photography. The price of the metal is subject to great variations, since a rainy season in the Caucasus will render larger amounts accessible to the miners, but, on the whole, the many applications which have been found for it have tripled its price in the last twenty years.

When special resistance to chemical or mechanical influences is required, as in standard meters for international reference, or points of fountain pens, the alloy with iridium is employed (*cf.* p. 240).

Compounds of Platinum. — **Platinous chloride** is made by passing chlorine over finely divided platinum at 240–250° or by heating chloroplatinic acid to the same temperature. It is greenish and insoluble in water, but forms with hydrochloric acid the soluble chloroplatinous acid H_2PtCl_4. The potassium salt of this acid K_2PtCl_4 is used in making platinum prints (*cf.* p. 635). Bases precipitate black **platinous hydroxide** $Pt(OH)_2$ which interacts with acids but not with bases. Gentle heating gives the **oxide** PtO and stronger heating the metal. With potassium cyanide and barium cyanide soluble **platinocyanides**, $K_2Pt(CN)_4,3H_2O$ and $BaPt(CN)_4,4H_2O$, are formed. These substances, when solid, show strong fluorescence, converting X-rays as well as ultra-violet rays into visible radiations. The barium salt is used to coat screens on which the shadows cast by X-rays are received.

Platinic chloride $PtCl_4$ may be made by treating the metal with *aqua regia* and heating the **chloroplatinic acid** H_2PtCl_6 so formed in a stream of chlorine at 360°. When dissolved in water, however, it gives a compound H_2PtCl_4O in which platinum is in the anion. Its solution deposits red, non-deliquescent crystals of $H_2PtCl_4O,4H_2O$.

Chloroplatinic acid forms reddish-brown deliquescent crystals $H_2PtCl_6,6H_2O$. With potassium and ammonium salts, it yields the sparingly soluble, yellow chloroplatinates K_2PtCl_6 and $(NH_4)_2PtCl_6$ (*cf.* p. 561), in solutions of which the platinum migrates towards the anode and silver salts precipitate Ag_2PtCl_6 and not silver chloride.

Bases interact with chloroplatinic acid, giving a yellow or brown precipitate of **platinic hydroxide** $Pt(OH)_4$. This substance interacts both with acids and with bases. In the former case the salts, which probably are formed, have not been isolated. In the latter case **platinates**, like $Na_2H_{10}Pt_3O_{12},H_2O$, have been obtained. Both sets of platinum compounds interact with hydrogen sulphide, giving the **sulphides**, PtS and PtS_2 respectively. These are black powders which dissolve in yellow ammonium sulphide solution, much as do the sulphides of gold, arsenic, and other metals, giving ammonium sulphoplatinates.

There are numerous complex compounds with ammonia representing both the platinous and platinic series. They resemble the ammonio-cobaltic compounds in their behavior.

INDEX

*** Acids are all listed under "acid" and salts under the positive radical.

ACCUMULATORS, 702
Acetylene, 496, 515
Acid, acetic, 498
 ionization of, 578
 antimonic, 716
 arsenic, 711
 arsenious, 711
 boracic, 527
 boric, 527
 bromic, 277
 carbolic, 441
 carbonic, 481
 chloric, 274
 chlorosulphuric, 399
 chlorous, 275
 chromic, 728
 disulphuric, 388
 dithionic, 398
 formic, 497
 hydrazoic, 422, 452
 hydriodic, 239, *see* Hydrogen iodide
 hydrobromic, 233, *see* Hydrogen bromide
 hydrochloric, 93, *see* Hydrogen chloride
 chemical properties, 185
 of constant boiling-point, 182
 hydrocyanic, 507
 hydrofluoboric, 527
 hydrofluoric, 242
 hydrofluosilicic, 521
 hypobromous, 276
 hypochlorous, 176, 267
 hyponitrous, 450
 hypophosphorous, 469
 hyposulphurous, 393
 iodic, 277
 metaphosphoric, 465, 468
 metastannic, 696
 muriatic, *see* Acid, hydrochloric
Acid, nitric, 93, 438
 fuming, 440
 oxidizing actions of, 446
 preparation, 439
 properties, 439
 nitrosylsulphuric, 383
 nitrous, 449
 orthophosphoric, 465, 466, 732
 oxalic, 499
 palmitic, 505
 pentathionic, 398
 perchloric, 276
 perchromic, 729
 periodic, 278
 permanganic, 743
 persulphuric, 397
 phosphorous, 469
 picric, 441
 pyrophosphoric, 467
 tannic, 754
 selenic, 402
 silicic, 523
 α-stannic, 696
 sulphuric, 93, 382
 chamber process, 383
 constitution, 391
 contact process, 380
 fuming, 388
 Nordhausen, 388
 properties, 387, 389
 uses, 393
 sulphurous, 393
 telluric, 403
 tetraboric, 528
 tetrathionic, 398
 thiosulphuric, 396
 trithionic, 398
Acidimetry, 351
Acids, 70, 92, 119, 281, 345
 activity of, *see* Chemical activity

Acids, complex, salts of, 360, 363, 536
constitution of, 470
dibasic, ionization of, 346, 374
ionic double decompositions of, 349
polythionic, 398
Activity, *see* Chemical activity
Adsorption, 476
Affinity, constant, 254
criticism of word, 29
inapt use of word, 110
see Chemical activity
Agar-agar, 313
Air, a mixture, 430
composition, 431
liquid, 434
solubility, 155
Albumins, 415
Alcohol, ethyl, 503
methyl, 503
Alizarine, 689
Alkalies, 348, 548
Allotropic modifications, 459
Alloys, 532
Alumina, 686
Aluminates, 685
Aluminium, 682
acetate, 688
carbide, 494
chloride, 684
hydroxide, 684
oxide, 686
sulphate, 686
sulphide, 687
Aluminothermy, 540
Alums, 547, 632, 687, 730, 741, 756
Amalgams, 532
Amethyst, 522
Ammonia, 417
Ammonia-soda process, 574
Ammonion, 568
Ammonium amalgam, 567
bromide, 564
carbamate, 566
carbonate, 565
chloride, 564
compounds, 420, 564
cyanate, 488, 566
hydroxide, 565
iodide, 564
nitrate, 451, 565
Ammonium sesquicarbonate, 566
sulphate, 566
sulphides, 566
sulphostannate, 697
thiocyanate, 566
Amorphous substances, 123, 139, 369, 475, 519
Analysis, application of ionic hypothesis in, 343
of compounds of carbon, 623
recognition of cations ("metals") in, 660
Analytical reactions, aluminium, 691
ammonium, 568
antimony, 720
arsenic, 720
barium, 612
bismuth, 720
cadmium, 652
calcium, 608, 612
chromium, 731
cobalt, 762
copper, 625
gold, 639
iron, 758
lead, 705
manganese, 745
magnesium, 645
mercury, 659
nickel, 762
potassium, 561
silver, 635
sodium, 577
strontium, 609, 612
tin, 697
zinc, 650
Anhydride, chromic, 728
hypochlorous, 267
iodic, 278, 279
nitric, 440
nitrous, 450
perchloric, 276
permanganic, 743
phosphoric, 464
sulphuric, 380
sulphurous, 378
Anhydrides, 71
mixed, 397, 463
various acids from one, 278
Anions, 322

Anode, 322
Antichlor, 397
Antimonites, 716
Antimony, 713
  nitrate, 716
  oxychloride, 715
  pentachloride, 715
  pentoxide, 715
  sulphate, 716
  sulphides, 716
  trichloride, 715
  trioxide, 715
Antimonyl compounds, 716
Apatite, 455
Aqueous tension, 82, 88, 116, 135
Aqua regia, 448
Aragonite, 591
Argentic compounds, *see* Silver
Argol, 501
Argon, 428, 434
Arsenic, 707
  pentoxide, 711
  sulphides, 712
  trichloride, 710
  trioxide, 710
Arsine, 709
  decomposition of, 252
Asbestos, 642
Asphalt, 492
Assaying, 639
Association, 242, 294
Atmosphere, 426
Atom, 196
  definition of, 218
Atomic hypothesis, 217
Atomic volume, 407
Atomic weight, definition of, 201
Atomic weights, 50
  determination of, 199
  table of, 203, 204, inside rear board
Attributes of bodies, 35
Avogadro's hypothesis, 131, 190, 288
Azurite, 616

BACTERIA, nitrifying, 438
Balanced actions, 248
Barium, 609
  carbonate, 610
  chlorate, 611
  chloride, 611
Barium, chloride, hydrated, 121
  chromate, 728
  dioxide, 611, *see* Peroxide
  hydroxide, 612
  nitrate, 612
  oxide, 611
  peroxide, 63, 303, 304, 611
    dissociation of, 257
  sulphate, 610
  sulphide, 610
Baryta-water, 612
Bases, 71, 119, 281, 348
  ionic double decompositions of, 350
  solubilities of, 544
Basicity, 358
Battery-cells, 666, *see* Cells
Battery, theory of, 667
Bauxite, 685
Bead tests, 468, 528, 731, 745
Beer, 502
Benzene, 497
Benzine, 492
Beryllium, *see* Glucinum, 641
Bessemer process, 749
Bicarbonates, *see* Hydrogen carbonates
Bichromates, *see* Dichromates
Bismuth, 717
  compounds, 718
Bisulphates, *see* Hydrogen sulphates
Bisulphites, *see* Hydrogen sulphites
Bleaching, 269, 394
  powder, 266, 602
Blue-stone (blue vitriol), 120, 625
Body, meaning of term, 34
Boiling-point of mixed liquids, 182, 503
Boiling-points, elevation of, 162
  of solutions, 162
Bone-ash, 456, 605
Bone black, 476
Borates, 528
Borax, 528
Boron, 526
  carbide, 529
  nitride, 529
  trichloride, 527
  trifluoride, 527
  trioxide, 529
Boyle's law, 84, 288
Brandy, 502
Brass, 619

Brimstone, 367
Brin's oxygen process, 63, 611
Bromine, 227
chemical properties, 230
physical properties, 229
preparation, 227
Bronze, 619
Brucite, 644

CADMIUM, 650
compounds, 651
Caesium, 563
Calamine, 646
Calcination, 456
Calcion, 608
Calcite, 591
Calcium, 589
carbide, 478, 602
carbonate, 591
chloride, 590
chromate, 727
fluoride, 591
hydride, 589
hydrogen sulphite, 395
hydroxide, 585, 596
nitrate, 602
oxalate, 597
oxide, 595
phosphates, 605
phosphide, 461
silicate, 606
sulphate, 603
sulphide, 604
Calculations, 58, 65, 91, 215
Calomel, 654
Calorie, 76
Cane-sugar, 500
Carbohydrates, 500
Carbon, 473
amorphous, 475
properties, 477
dioxide, 479
properties, 480
disulphide, 488
monoxide, 485
properties, 486
Carbonates, 482
Carbonates, acid, *see* Hydrogen carbonates
Carbonyl chloride, 487
Carborundum, 520
Carnallite, 551, 642, 643
Cassiterite, 693
Catalytic action, 75, 96, 111, 508
Cathode, 322
Cations, 322
Cause, in Science, 30
Caustic potash, 552
Cell, Bunsen, 673
Daniell, 672
dichromate, 673
dry, 673
gravity, 672
Leclanché, 673
storage, 702
Cells, battery, 666
concentration, 673
Cellulose, 500
Cement, 597
Cerium, 510, 682, 705
Chalk, 591
Chalybeate water, 483
Chance's process, 574
Characteristics of chemical phenomena, 5, 16, 17, 26, 27, 41, 48
Charcoal, 476
properties, 476
Charles' law, 85, 87
Chemical activity, cause of, 28
measurement of, 28, 79, 111, 678, 679
of acids, 347, 356, 679
Chemical change, spontaneously progressing, 27
varieties of, 14, 99, 121, 176, 181, 187, 360 (ionic), 397, 520
Chemical relations of elements, 177, 226, 719
Chemistry, methods of work in, 36
Chinese white, 648
Cinnabar, 653
Chlorates, 272
Chlorides, electrolysis of, 169
interaction with acids, 179
solubility, 185
Chlorine, 168
bleaching action, 177
chemical properties, 174
chemical relations, 177
dioxide, 275

Chlorine, physical properties, 173
preparation, 168
test for, 175
uses, 177
Chloroform, 494
Choke-damp, 493
Chrome-alum, 730
Chromic acetate, 731
anhydride, 728
chloride, 729
oxide, 730
hydroxide, 729
sulphate, 730
Chromites, 729
Chromium, 722
trioxide, 728
Chromous compounds, 731
Chromyl chloride, 728
Clay, 525, 689
Coal, 477
Cobalt, 758
complex compounds, 760
zincate, 648
Cobaltic compounds, 760
Cobaltous compounds, 759
Coke, 475
Colloidal solution, 523
Colloids, 524
Columbium, 721
Combination, 14
Combining proportions, measurement of, 43
Combining weights, 46
law of, 48
Combustion, 71
Common ion, effect of adding, 580
Complex cations, 534, 614, 622, 661, 662
cadmium, 652
chromium, 729, 730
cobalt, 759, 760
copper, 620, 622, 623, 625
mercury, 659
nickel, 761
platinum, 766
silver, 629, 631
zinc, 648
Component, definition of, 34
Compound, 15
Compounds, binary, 103
molecular, 123, 443
Concentration, molar, 250
molecular, law of, 252
illustration of law of, 394
of gases, 80
Conditions, 35, 52
Conductivity, electrical, 325
Condy's disinfecting fluid, 743
Congo red, 355, 689
Conservation of mass, 17
Constant, depression, 291
ionization, 297
heat summation, law of, 78
Constituent, definition of, 34
Constitution of acids, 470
of substances, 104, 224, 279, 308, 391, 421, 441, 451, 466
Copper, 615
acetylene, 496, 516
properties, 618
Corpuscles, 222, 735
Couples, electrical, 96, 673
Corrosive sublimate, 655
Crayon, 591
Cream of tartar, 502
Critical phenomena, 133
Cryolite, 683
Crystal, forms, 137
structure, 140
Crystallization, water of, 123, 181, *see* Hydrates
Cupric acetate, 624
bromide, 621
ionization of, 335
carbonate (basic), 623
chloride, 619
cyanide, 624
ferrocyanide, 286, 299, 757
hydroxide, 623
iodide, 621
nitrate, 623
oxide, 43, 622
sulphate, 624
hydrated, 120, 122
sulphide, 625
Cuprous chloride, 620
cyanide, 624
iodide, 621
oxide, 622
sulphide, 625
Cyanogen, 507

DALTON'S law of partial pressures, 88
Deacon's process, 170
Decomposition, 15
  potentials, 324, 675
Decrepitation, 556
Definite proportions, law of, 41
Deliquescence, 162
Densities of gases, 193
  measurement of, 89, 90
Densities of solutions, 164
"Derived from," meaning of term, 278
Dextrose, 500
Dialysis, 523
Diamond, 474
Dichromates, chemical properties of, 725
Diffusion, in gases, 107
  in liquids, 136
Dilution formula, Ostwald's, 298
Dimorphous substances, 369
Discharging potentials, 324, 675
Displacement, 95, 99
  ionic, 342, 361
Dissociation, 121
  hydrolytic, 181, *see* Hydrolysis
  in solution, proofs of, 281, 289, 292, 293
  of compounds (by heat), 208
  pressure, 257
Distillation, 38
  fractional, 399, 492
  in vacuo, 276, 471
Dolomite, 642
Double decomposition, 15
Dulong and Petit's law, 211
Dyeing, 688

EARTHENWARE, 689
Efflorescence, 121, 123, 162
Electrolysis, 310, 675
  of chlorides, 169
Electrolytes, 296, 310
Electromotive chemistry, 664
  force, 665
  series, 361, 670, 676
Electrons, 222, 735
Electroplating, 632
Element, definition of, 31, 32
  not same as simple substance, 32, 57
Elements, base-forming, *see* Elements metallic
  chemical relations of, 177, 226, 719
  metallic, 119, 337, 404, 533
    classification of, 537
Elements, molecular weights of, 206
  negative, 322, 405
  non-metallic, 119, 337, 405, 534
  positive, 322, 404
  quantities of terrestrial material, 33
Endothermal actions, 27
Energy, and chemical change, 19, 28
  chemical, 25
  conservation of, 23
  definitions of, 23, 24
  factors of, 677
  free or available, 26
  units employed in measuring, 25
Enzymes, 501
Epsom salts, 644
Equations, 54
  making of, 55, 69, 208, 274, 447
  molecular, 208
Equilibria, displacement of, 257
Equilibrium, 117, 135
  chemical, 246
  ionic, 297
    considered quantitatively, 578
Equivalents, 49, 102
Esters, 504
Ether, 147, 506
  luminiferous, 24
Ethyl acetate, 504
  sulphate, 504
Ethylene, 495
  bromide, 496
Excess, meaning of term, 43
Exothermal actions, 27
Explanation, its nature, 10
Explosives, 452

FACTORS of energy, 77, 677
Fat, 505
Fehling's solution, 623
Fermentation, 501
Ferrates, 758
Ferric, compounds, 754, 755, 756
  thiocyanate, 250, 757
Ferrous, compounds, 753, 754
  sulphide, 12, 42, 371

Fertilizers, 415, 467, 605
Filtrate, 11
Fire-damp, 493
Flame, 509
  Bunsen, 511, 512
Flame, chemical changes in, 513
Flash-light powder, 643
Fluorine, preparation, 240
  properties, 241
Fluorite, 591
Flux, 529
Formulæ, 53
  graphic, *see* Constitution of substances
  making of, 55, *see* Equations
  molecular, of compounds, 204
    of simple substances, 205
  structural, *see* Constitution of substances
Franklinite, 646, 756
Freezing mixtures, 164
Freezing-point, depression constant, 291, 294
Freezing-points, depression of, 163, 290
  of solutions, 163, 290
Furnace, blast, 748
  electric, 457, 479
  reverberatory, 572

GALENA, 698, 705
Gallium, 681
Garnet, 525, 683
Gas, illuminating, composition of, 513
Gases, densities of, 193
  drying of, 100
  liquefaction of, 432
  purification of, 100
  solubility of, 153
Gasoline, 492
Gay-Lussac's law, *see* Charles' law
  of combining volumes, 125
Germanium, 692
Glass, 606
Glauber's salt, 120, 158, 160, 576
Glucose, 500
Glycerine, 503
Gold, 635
  compounds of, 638
Gram-molecular volume, 199
Grape-sugar, 500
Graphite, 475

Green fire, 611
Greenockite, 650
Gun-cotton, 441, 452, 504
Gunpowder, 557
Gypsum, 603

HALOGEN family, 226, 243, 279
Heat, of fusion, 115
  of solution, 164
  of vaporization, 118
Heavy-spar, 610
Helium, 436, 563, 736
Homologous series, 491
Hydrargyllite, 685
Hydrates (hydroxides), 120
  (substances containing water of crystallization), 120
  of salts, composition of, 545
  vapor tension of, 121
Hydrazine, 422
Hydrion, properties of, 346
Hydrocarbons, 490
  properties of, 493
Hydrogele, 523
Hydrogen, 92
  chemical properties, 108
  physical properties, 106
  preparation, 93, 95, 97, 99, 362
  bromide, preparation, 230
    properties, 232
  chloride, chemical properties, 183
    composition, 183
    physical properties, 182
    preparation, 178, 585
  fluoride, physical properties, 241
    preparation, 241
  iodide, dissociation of, 254
    interaction with sulphuric acid, 237
    preparation, 237
    properties, 239
  pentasulphide, 376
  peroxide, 126, 303
  selenide, 401
  sulphate, properties, 387
  sulphide, 371
    chemical properties, 373, 374
  telluride, 403
Hydrolysis, definition of, 181
  of halogen compounds, 534
  of salts, 344

Hydrosole, 523
Hydroxidion, properties of, 349
Hydroxylamine, 423
Hypobromites, 276
Hypochlorites, 265
Hypotheses, formulative, 141
Hypotheses, stochastic, 142
Hypothesis, 128
  atomic, 217
  Avogadro's, 131, 190
  corpuscular, 222
  ionic, 296, 317
  kinetic-molecular, 128
  molecular applied to solutions, 150

ICE, 115
Iceland spar, 591
Identification, means of, 35, 39
Illuminating-gas, composition of, 513
Indicators, 353, 355
Indigo, 688
Indium, 681
Ink, 754
Insoluble compounds, theory of precipitation of, 581, 585, 601, 644
  theory of solution of, 585, 598, 601, 621, 644, 648
Internal rearrangement, 15, 488
Inversion, 500
Iodine, 233
Iodine, chlorides, 244
  pentoxide, 278, 279
  preparation, 234
  properties, 235
  uses, 236
Iodimetry, 236
Iodoform, 494
Ion, common, effect of adding, 580
  definition of, 321
  product, 583
Ionic concentration, 585
  hypothesis, 296, 317
    objections to, 319
Ionization, degrees of, 329
Ionogens, 296
Iridium, 764
Iron, 746
  alum, 756
  carbonyls, 757
  cast, 748, 751
Iron, chemical properties, 752
  cyanides, 756
  wrought, 749
  see Ferrous and Ferric
Isomers, 262, 488, 696
Isomorphism, 545

KAINITE, 360, 559
Kalion, 561
Kaolin, 525, 689
Kerosene, 492
Kieserite, 645
Krypton, 437

LAKES, 689
Lanthanum, 681, 682
Lampblack, 476
Law, definition of, 7
  Dulong and Petit's, 211
  Faraday's, 315
  Gay-Lussac's, 125
  Henry's, 154
  Le Chatelier's, 260
  misconceptions in regard to ture of, 7
  of combining weights, 48
  of mobile equilibrium, 260
  of partition, 155
  periodic, 410
  van 't Hoff's, 260
Laws, two kinds of, 191
Lead, 698
  acetate, 704
  carbonate, 704
  chlorides, 700
  chromate, 727
  hydroxide, 701
  iodide, 700
  nitrate, 703
  oxides, 700, 701, 702
  sugar of, 704
  sulphate, 704
  sulphide, 705
Le Blanc soda process, 572
Light, *see* Photochemistry
Lignin, 395
Lime, chloride of, *see* Bleaching
  milk of, 596
  superphosphate of, 467, 605
Limestone, 591, 592, 595

Liquefaction of gases, 432
Litharge, 700
Lithium, 577
Litmus, 70, 355
Lodestone, 756
Lunar caustic, 631

MAGNALIUM, 683
Magnesia alba, 644
Magnesium, 642
  ammonium arsenate, 645
  carbonate, 644
  chloride, 643
  hydroxide, 644
  oxide, 643
  phosphates, 645
  sulphate, 644
  sulphide, 645
Malachite, 616
Manganates, 737, 741
Manganese, 737
  dioxide, 63, 171, 398
  oxides of, 738
Manganic compounds, 737, 740
Manganites, 737, 741
Manganous compounds, 737, 739, 740
  sulphate, 739
Marsh gas, 493, 709, 714
Mass action, 250
Massicot, 700
Matches, 460
Matrix, 367
Matter, 23
Mercur-ammonium compounds, 659
Mercuric, cyanide, 658
  fulminate, 658
  oxide, 12, 61
  thiocyanate, 658
Mercury, 652
  chlorides, 654
  iodides, 656
  nitrates, 657
  oxides, 656
  sulphides, 657
Metallic elements, 119, 337, 404, 534
Metals, electrical conductivity of, 532
  extraction from ores, 540
  hydroxides of, 541
  occurrence of, 539
  oxides of, 541
Metals, physical properties of, 530
  see Metallic elements
"Metals," recognition of, in analysis, 660
Metastable condition, 159
Methane, 493
Methyl, formate, 504
  orange, 355
Mica, 525
Microcosmic salt, 467, 567
Migration, ionic, 312
  speed of, 314
Minium, 701
Mobile equilibrium, law of, 260
Mohr's salt, 754
Molar, volume, 199
  weight, 197
Mole, 197
Molecular, compounds, 443
  magnitudes, 140
  weight, chemical unit of, 196
  weights, 191
    in solution, 289, 292, 305
    of elements, 206
    rule for measuring, 197, 199, 210
Molecule, the chemical, 198, 296
Molybdenum, compounds of, 732
Mordants, 689
Mortar, 597
Multiple proportions, law of, 41

NAPHTHA, 492
Nascent state, 272, 423, 446
Natrion, 577
Neon, 437
Neodymium, 682
Nernst lamp, 706
Nessler's reagent, 659
Neutralization, 266, 351
  theory of, 353
  thermochemistry of, 357
  volume change in, 358
Nickel, 700
  carbonyl, 762
  compounds, 7[illegible], 762
Niobium, 721
Nitrates, 442
Nitric oxide, 442
Nitrites, 449
Nitrogen, 62, 415

Nitrogen, chloride, 424
  iodide, 425, 452
  oxides, 438
  oxygen acids of, 438
  tetroxide, 444
Nitroglycerine, 441, 452, 504
Nitrosyl chloride, 448
Nitrous oxide, 450
Nomenclature, acids and salts, 263
  ionic hypothesis, 296, 321
Non-ionic actions, 364
Non-metallic elements, 119, 405, 534

OCTANTS, law of, 406
Oleum, 388
Orpiment, 712
Osmium, 763
Oxidation, 70, 72, 110, 454
Oxides, 70
Oxygen, 61
  atomic weight why *sixteen*, 196
  chemical properties, 67
  physical properties, 66
  preparation, 63
Ozone, 300
Ozocerite, 492

PALLADIUM, 764
Paper, manufacture of, 395, 501, 686
Paris green, 624, 712
Parke's process, 627
Pattinson's process, 627
Pearl ash, 558
Perfect gas, 85
Periodates, 278
Periodic system, 407
  applications of, 412
Peroxides, 308
Petroleum, 491
  ether, 492
Pewter, 694
Phase rule, 592
Phases, 156
Phenol, 441
Phenolphthaleïn, 355
Phlogiston, 9
Phosgene, 487
Phosphine, 461, 469
Phosphonium compounds, 462
Phosphorus, 455
Phosphorus, acids of, 465
  halides, 462
  oxides, 464
  pentachloride, 462
    dissociation of, 255
  pentoxide, 464
  preparation, 455
  properties, 457
  red, 457
  sulphides, 471
  trichloride, 462
  trioxide, 464
  uses, 460
  yellow, 457
Photochemistry, 458, 484, 633
  of plants, 483
Photography, 633
Physics needed in the study of chemistry, 39, 65
Pink-salt, 695
Plaster of paris, 603
Platinum, 765
  compounds of, 766
Plumbates, 702
Plumbic, *see* Lead.
Polarization, 324, 675
Polymerization, 242
Polysulphides, 376
Porcelain, 690
Potassamide, 420
Potassium, 549
  aluminium sulphate, 687
  arsenite, 712
  bromate, 556
  bromide, 552
  carbonate, 557
  chlorate, 64, 275, 555, 583
  chloride, 550
  chromate, 723
  cyanate, 507, 559
  cyanide, 558
  dichromate, 725
  ferrate, 758
  ferricyanide, 757
  ferrocyanide, 756
  fluorides, 552
  hydride, 550
  hydrogen sulphate, 560
    sulphide, 560
    tartrate, 561

Potassium, hydroxide, 552, 558
  iodate, 556
  iodide, 551
  metantimoniate, 716
  nitrate, 556
  oxides, 555
  percarbonate, 558
  perchlorate, 556
  permanganate, 742
  plumbate, 702
  pyrosulphate, 560
  sulphate, 559
  sulphides, 560
  thiocyanate, 508, 559
  zincate, 648
Potential, chemical, 678
  differences (anions), 676
    (cations), 670
  discharging, 675
Precipitate, 13
Precipitation, in ionic actions, 339, 350
  rule for, 587
  rule of (Berthollet's), 259
Pressure, dissociation, 257
  osmotic, 151, 283, 299
  partial, 88
  solution, 152
  vapor, 115, 135
Principles, summary of, 188, 262
Properties, specific, 35
Proustite, 626, 713
Prussian blue, 757
Pumice-stone, 525
Pure, chemically, definition of, 34
Putrefaction, 501
Pyrargyrite, 626, 717
Pyrite, 42, 756
Pyrosulphates, 388

Quartation, 532
Quartz, 522
Quicklime, 592, 595
Quicksilver, 653

Radicals, 93
  organic, 494, 499
  valence of, 104
Radio-activity, 783
Radium, 783

Realgar, 712
Red, fire, 658
  heat, temperature corresponding to, 73
  lead, 701
Reduction, 72, 110
Reversible actions, 176, 179, 237, 246
Rhodium, 764 264
Rhombohedron, 14
Roasting, 378
Rock crystal, 522
Rouge, 755
Rubidium, 563
Ruthenium, 763

Salammoniac, 564
Saltpeter, 438, 569
Salts, 264, 281, 337
  acid, 358
  basic, 359
  composition of hydrates of, 545
  definition of term, 365
  double, 360
  general methods of making, 542
  ionic double decompositions of, 337
  mixed, 359
  nomenclature of, 263
  of complex acids, 360, 363
  of hydrogen, 345
  of hydroxyl, 348
  precipitation of, 339, 585
  solubilities of, 157, 544
Samarium, 681
Sand, 522
Saponification, 505
Scandium, 681
Scheele's green, 624, 712
Schlippe's salt, 717
Sciences, classification of, 3
Scientific method, 4, 6, 10, 16, 17, 23, 28–30, 128, 141, 191
Selenium, 401
Semi-permeable partitions, 284, 299
Shoenite, 559
Silicates, 524
Silicon, 518
  carbide, 520
  dioxide, 522
  hydride, 519
  tetrachloride, 520

Silicon, tetrafluoride, 521
Silver, 626
  arsenate, 632
  carbonate, 631
  chloride, 14
  chromate, 632, 728
  complex compounds of, 629
  cyanide, 630, 632
  halides, 629, 633
  nitrate, 13, 631
  orthophosphate, 632
  oxides of, 630
  -plating, 632
  properties, 628
  sulphate, 632
  sulphide, 632
  thiosulphate, 630
Simultaneous actions, 231, 272, 275
Slag, 540
Soap, 505
Soda, crystals, 573
  washing, 573
Sodium, 569
  aluminate, 99, 685
  amalgam, 569
  arsenite, 712
  carbonate, manufacture, 571
    properties, 575
  chloride, 13, 570
  chromate, 724
  dichromate, 725
  hydride, 569
  hydrogen carbonate, 575
  periodate, 279
  hydroxide, 570
  hyposulphite, 393
  "hyposulphite," *see* Thiosulphate
  nitrate, 14, 571
  nitrite, 571
  oxide, 571
  pentasulphide, 376
  peroxide, 303, 308, 571
  phosphates, 577
  plumbite, 701
  pyroantimoniate, 577, 716
  silicate, 577
  stannate, 696
  sulphate, 576
    hydrated, 120, 158, 160
  tetraborate, 528, 577
Sodium, thiosulphate, 576
  zincate, 99
Soldering, 421
Solubility, curves of, 157, 158
  data, 147, 154, 157, 531
  independent, 153
  influence of temperature on, 156
  limits of, 146
  measurement of, 147
  of gases, 153
  product, 583
  separation of substances by, 273
Solution, 145
  definition of, 165
  heat of, 164
  in two solvents, 155
  of insoluble substances, 585, 598
    601, 621, 644, 648
  scope of word, 146
Solutions, boiling-point of, 162
  densities of, 164
  freezing-points of, 163
  general properties of, 145
  is-osmotic, 285
  molar, 149
  normal, 148
  saturated, 148, 153, 161, 581
  solid, 146
  standard, 236
  supersaturated, 159
  vapor tension of, 161
Solution tension, hypothesis of, 670
Solvay soda process, 574
Specific heats of elements, 211
Spectroscope, 561
Spectrum, 562
Speed of reaction, 111, 251, 394
  affected by, catalysis, 75
    concentration, 74, 250, 394
    solution, 76, 283
    temperature, 73
Spinelles, 686
Spirit of hartshorn, 418
Stable, meaning of term, 119
Stannous, *see* Tin.
Starch, 500
Steam, 115
Stearin, 506
Steel, properties of, 750
  theory of tempering, 750

Stibine, 714
Stibnite, 714
Storage battery, 702
Strontium, chloride, 608
hydrated, 121
chromate, 728
compounds, 608
peroxide, 305
Structure, molecular, 213, 224, *see* Constitution.
Sublimation, 235, 463
Substance, meaning of term, 30, 32, 35
Substitution, 176
Suint, 557
Sulphantimoniates, 717
Sulphantimonites, 717
Sulpharsenates, 712
Sulpharsenites, 712
Sulphates, 390
acid, 390, *see* Hydrogen sulphates
Sulphides, 375
relative solubilities of, 651
Sulphites, 395
Sulphocyanates, *see* Thiocyanates
Sulphostannate, 697
Sulphur, 11, 367
chemical properties, 370
chemical relations, 377
crystalline form, 11
dioxide, 378
family, chemical relations of, 403
monochloride, 398
oxides of, 378
oxygen acids of, 381
physical properties, 368
tetrachloride, 399
trioxide, 380
Sulphuretted hydrogen, *see* Hydrogen sulphide
Sulphuryl chloride, 399
Summary of principles, 188, 262
Superphosphate of lime, 467, 605
Sylvite, 551
Symbols, 53
Synthesis, 473
System, meaning of term, 158

Tantalum, 721
Tartar-emetic, 716
Tellurium, 402
Temperature, critical, 134
Tests, 99
Thallium, 681
Theory, *see* Hypothesis
Thermochemistry, 76, 233, 271, 307, 357
Thionyl chloride, 399
Thiocyanates, 250, 508, 559, 757
Thorium, 510, 705
Tin, 693
bromide, 695
chloride, 694, 695
hydroxide, 696
oxides, 696
-stone, 693
sulphides, 697
Titanium, 705
Titration, 352
Touch-paper, 557
Transformation by steps, 453
Transition points, 115, 118, 369, 594
Triethylamine, 156
Tungsten, 732
Turnbull's blue
Turquoise, 683
Type-metal, 699

Ultramarine, 690
Units, 25, 58, 533
electrical, 665
Uranium, compounds, 733
Urea, 487

Valence, 101
definitions of, 102, 103, 106
exceptional, 106
multiple, 105
of radicals, 104
Vanadium, 721
Vapor, densities, 90
pressure, 115, 135
tension of solutions, 161
Velocity, *see* Speed of reaction
Venetian red, 755
Verdigris, 624
Vermilion, 658
Vinegar, 498
Vitriol, blue, 120, 625
green, 754
oil of, *see* Acid, sulphuric
white, 649

Vitriols, 546, 649
Volume, atomic, 407
  molar, 199
Volumetric analysis, 353

WATER, 113
  chemical properties, 118
  composition, 124
  electrolysis, 676
  gas, 485
  hard, 113, 594
  ionization of, 331
  mineral, 113
  of crystallization, *see* Hydrates
  physical properties, 114
  purification, 113
Weight, molar, 197
Weights, atomic, *see* under Atomic weights
  molecular, *see* under Molecular weights
Weldon process, 741
Welsbach mantles, 705
Whiskey, 477, 502
White lead, 704
Wine, 501

XENON, 437

YTTERBIUM, 681
Yttrium, 681

ZINC, 646
  acetate, 649
  -blende, 646, 649
  carbonate, 649
  chloride, 647
  hydroxide, 648
  oxide, 646, 648
  sulphate, 649
  sulphide, 649
  -white, 648
Zincates, 648
Zirconium, 705